PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 7 : **C03C 25/10, C08J 5/08, H05K 1/03**	A1	(11) International Publication Number: **WO 00/21900** (43) International Publication Date: 20 April 2000 (20.04.00)

(21) International Application Number: PCT/US99/21443

(22) International Filing Date: 8 October 1999 (08.10.99)

(30) Priority Data:

09/170,578	13 October 1998 (13.10.98)	US
60/133,076	7 May 1999 (07.05.99)	US
60/133,075	7 May 1999 (07.05.99)	US
60/146,337	30 July 1999 (30.07.99)	US

(71) Applicant *(for all designated States except US)*: PPG INDUSTRIES OHIO, INC. [US/US]; 3800 West 143rd Street, Cleveland, OH 44111 (US).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: NOVICH, Bruce, E. [US/US]; 1035 Highmont Road, Pittsburgh, PA 15232 (US). ROBERTSON, Walter, J. [US/US]; 28 Shannopin Drive, Pittsburgh, PA 15202 (US). VELPARI, Vedagiri [US/US]; 230 Old Haymaker Road, Monroeville, PA 15146 (US). LAMMON-HILINSKI, Kami [US/US]; 617-2 Center Avenue, Aspinwall, PA 15215 (US). LAWTON, Ernest, L. [US/US]; 3432 Kilcash Drive, Clemmons, NC 27012 (US).

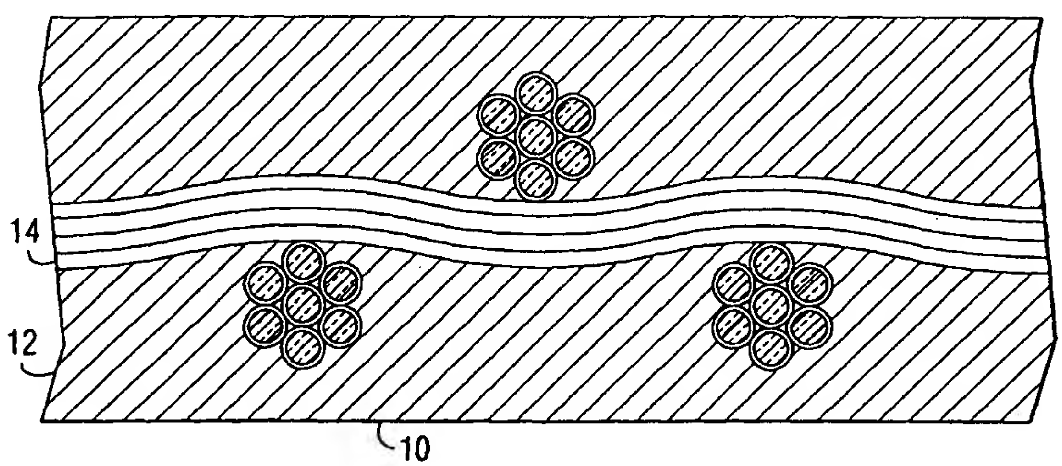
(74) Agents: SIMINERIO, Andrew, C.; PPG Industries, Inc., One PPG Place, Pittsburgh, PA 15272 (US) et al.

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published

With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: GLASS FIBER-REINFORCED PREPREGS, LAMINATES, ELECTRONIC CIRCUIT BOARDS AND METHODS FOR ASSEMBLING A FABRIC



(57) Abstract

One aspect of the present invention is a prepreg for an electronic support, the prepreg comprising: (a) a polymeric matrix material; and (b) a fabric comprising a strand comprising glass fibers, at least a portion of the fabric having a coating which is compatible with the polymeric matrix material, the prepreg having a drill tip percent wear of no greater than about 32 percent, as determined after drilling 2000 holes through a stack of 3 laminates, each laminate including eight of the prepregs, at a hole density of 62 holes per square centimeter (400 holes per square inch) and a chip load of 0.001 with a 0.46 mm (0.018 inch) diameter tungsten carbide drill. The present invention also provides a laminate incorporating the prepreg. Another aspect of the present invention is a prepreg for an electronic support, the prepreg comprising: (a) a polymeric matrix material; and (b) a woven reinforcement fabric comprising glass fibers, at least a portion of the fabric having a coating which is compatible with the polymeric matrix material, the prepreg having a deviation distance of no greater than about 36 micrometers, as determined after drilling 2000 holes through a stack of 3 laminates at a hole density of 62 holes per square centimeter (400 holes per square inch) and a chip load of 0.001 with a 0.46 mm (0.018 inch) diameter tungsten carbide drill. The present invention also provides a laminate incorporating the prepreg.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania
AM	Armenia
AT	Austria
AU	Australia
AZ	Azerbaijan
BA	Bosnia and Herzegovina
BB	Barbados
BE	Belgium
BF	Burkina Faso
BG	Bulgaria
BJ	Benin
BR	Brazil
BY	Belarus
CA	Canada
CF	Central African Republic
CG	Congo
CH	Switzerland
CI	Côte d'Ivoire
CM	Cameroon
CN	China
CU	Cuba
CZ	Czech Republic
DE	Germany
DK	Denmark
EE	Estonia
ES	Spain
FI	Finland
FR	France
GA	Gabon
GB	United Kingdom
GE	Georgia
GH	Ghana
GN	Guinea
GR	Greece
HU	Hungary
IE	Ireland
IL	Israel
IS	Iceland
IT	Italy
JP	Japan
KE	Kenya
KG	Kyrgyzstan
KP	Democratic People's Republic of Korea
KR	Republic of Korea
KZ	Kazakstan
LC	Saint Lucia
LI	Liechtenstein
LK	Sri Lanka
LR	Liberia
LS	Lesotho
LT	Lithuania
LU	Luxembourg
LV	Latvia
MC	Monaco
MD	Republic of Moldova
MG	Madagascar
MK	The former Yugoslav Republic of Macedonia
ML	Mali
MN	Mongolia
MR	Mauritania
MW	Malawi
MX	Mexico
NE	Niger
NL	Netherlands
NO	Norway
NZ	New Zealand
PL	Poland
PT	Portugal
RO	Romania
RU	Russian Federation
SD	Sudan
SE	Sweden
SG	Singapore
SI	Slovenia
SK	Slovakia
SN	Senegal
SZ	Swaziland
TD	Chad
TG	Togo
TJ	Tajikistan
TM	Turkmenistan
TR	Turkey
TT	Trinidad and Tobago
UA	Ukraine
UG	Uganda
US	United States of America
UZ	Uzbekistan
VN	Viet Nam
YU	Yugoslavia
ZW	Zimbabwe

GLASS FIBER-REINFORCED PREPREGS, LAMINATES, ELECTRONIC CIRCUIT BOARDS AND METHODS FOR ASSEMBLING A FABRIC

Cross Reference to Related Applications

This patent application is a continuation-in-part of U.S. Patent Application Serial No. 09/170,578 of B. Novich et al. entitled "Glass Fiber-Reinforced Laminates, Electronic Circuit Boards and Methods for Assembling a Fabric", filed October 13, 1998, which is a continuation-in-part of U.S. Patent Application Serial No. 09/130,270 of B. Novich et al. entitled "Glass Fiber-Reinforced Laminates, Electronic Circuit Boards and Methods for Assembling a Fabric", filed August 6, 1998, now abandoned, which is a continuation-in-part application of U.S. Serial No. 09/034,525 of B. Novich et al. entitled "Inorganic Lubricant-Coated Glass Fiber Strands and Products Including the Same" filed March 3, 1998, now abandoned. This application is also a continuation-in-part of U.S. Patent Application Serial No. 09/170,780 of B. Novich et al. entitled "Inorganic Lubricant-Coated Glass Fiber Strands and Products Including the Same" filed October 13, 1998, which is a continuation-in-part application of U.S. Patent Application Serial No. 09/034,525 of B. Novich et al. entitled "Inorganic Lubricant-Coated Glass Fiber Strands and Products Including the Same" filed March 3, 1998, now abandoned. This application is also a continuation-in-part of U.S. Patent Application Serial No. 09/170,781 of B. Novich et al. entitled "Glass Fiber Strands Coated With Thermally Conductive Inorganic Solid Particles and Products Including the Same" filed October 13, 1998, which is a continuation-in-part application of U.S. Application Serial No. 09/034,663 filed March 3, 1998, now abandoned.

This patent application is related to U.S. Patent Application Serial No. 09/170,579 of B. Novich et al. entitled "Methods for Inhibiting Abrasive Wear of Glass Fiber Strands" filed October 13, 1998, which is a continuation-in-part application of U.S. Patent Application Serial No. 09/034,078 filed March 3, 1998, now abandoned; U.S. Patent Application Serial No. 09/170,566 of B.

Novich et al. entitled "Impregnated Glass Fiber Strands and Products Including the Same" filed October 13, 1998, which is a continuation-in-part application of U.S. Patent Application Serial No. 09/034,077 filed March 3, 1998, now abandoned; and U.S. Patent Application Serial No. 09/170,565 of B. Novich et al. entitled "Inorganic Particle-Coated Glass Fiber Strands and Products Including the Same" filed October 13, 1998, which is a continuation-in-part application of U.S. Patent Application Serial No. 09/034,056 filed March 3, 1998, now abandoned.

This application claims the benefit of U.S. Provisional Application Nos. 60/133,075, filed May 7, 1999; 60/133,076, filed May 7, 1999, and 60/146,337, filed July 30, 1999.

Field of the Invention

This invention relates generally to reinforced laminates for electronic circuit boards and, more particularly, to laminates containing woven fabrics of glass fibers having a coating which is compatible with laminate matrix resins and provides improved drilling properties in the laminate.

Background of the Invention

Electronic circuit boards are typically formed from laminated layers of resin impregnated fabric composed of reinforcing fibers, such as glass fibers, which provide dimensional stability to the board to maintain the integrity of the electronic circuits mounted thereon. Holes are formed in the laminate by drilling through the layers of the laminate or support to interconnect circuits positioned along different planes of the laminate. It has been observed that the hardness of the glass fibers in the laminate and the heat generated during the drilling operation can accelerate the wear of the drill bit. As a result, the drill bit will drill fewer holes before drill replacement and/or resharpening of the drill tip, and will have a shorter overall useful tool life. In addition, it has been observed that the accelerated drill tip wear also effects the locational

accuracy of the holes, and in particular the exit end of the hole drilled through a laminate.

Typically, the surfaces of glass fibers forming these reinforcing fabrics of the laminates are coated with a sizing composition in the fiber forming process to protect the fibers from abrasion during subsequent processing. For example, starch and oil-based sizing compositions are used to protect fibers from interfilament and equipment abrasion during fabric weaving which can contribute to fiber breakage. Organic lubricants, such as alkyl imidazoline derivatives and amide substituted polyethylene imines, have been added to sizing compositions to reduce abrasion. However, such organic lubricants can deteriorate during subsequent processing or cause undesirable side reactions with other sizing and matrix material components. In addition, many commonly used sizing components can adversely affect adhesion between the glass fibers and the laminate matrix material, e.g., starches, which are commonly used as film formers in textile sizings, are generally not compatible with the laminate resin matrix material. To avoid incompatibility between the glass fibers and matrix materials, the coating or sizing composition is typically removed from the woven cloth prior to lamination by thermally decomposing the components of the sizing (heat treatment or de-oiling) or by washing with water or other solution. A conventional heat cleaning process involves heating the cloth at 380°C for 60-80 hours. The cleaned cloth is then re-coated with a silane coupling agent to improve adhesion between the glass fiber and the matrix resin.

The strength of the glass fibers, and more particularly the flexural strength of the laminate, can be greatly reduced by these heat cleaning processes. Heat cleaning of high silica content glass fibers, such as D-glass, S-glass and Q-glass, is particularly undesirable because of strength loss and discoloration.

Many coating compositions for glass fibers which require heat or water cleaning prior to use as a reinforcement in a composite or laminate are

disclosed in the art. Japanese Patent Application No. 9-208,268 discloses a cloth having yarn formed from glass fibers coated immediately after spinning with starch or a synthetic resin and 0.001 - 20.0 weight percent of inorganic particles such as colloidal silica, calcium carbonate, kaolin and talc. Heat or water de-oiling is required prior to formation of a laminate.

U.S. Patent No. 5,286,562 discloses a textile strand for screen products which is weaveable on air jet looms having a coating of at least 45 weight percent wax, lubricants, polyvinyl pyrrolidone and organo silane coupling agents. U.S. Patent No. 5,038,555 discloses twisted bundles of glass fibers for screen products which are coated with an aqueous chemical treating composition having an epoxy film former, emulsifier, lubricant, organo functional metallic coupling agent, polyvinyl pyrrolidone, polyethylene and water.

To avoid heat cleaning glass fiber cloth, Japanese Patent Application No. 8-119,682 discloses a primary sizing agent for glass fibers containing a water-soluble epoxy resin and having a pH of 5.5 to 7.5, which facilitates removal of the sizing with water. Similarly, U.S. Patent No. 5,236,777 discloses methods for producing glass cloth for reinforcing a resin by coating the glass yarns with a primary sizing having at least one water-soluble film-forming agent selected from the group consisting of an amine-modified epoxy resin, an ethylene oxide-added epoxy resin and ethylene oxide-added bisphenol A, silane coupling agent and lubricant, water washing the yarns to reduce the amount of primary sizing to less than 0.25 weight percent LOI and treating with a secondary sizing agent. Japanese Patent Application No. 9-268,034 discloses binders for twist-free glass fiber yarn including a water-soluble urethane compound and/or a water-soluble epoxy product modified by addition reaction with a polyhydric alcohol.

U.S. Patent No. 4,933,381 discloses a resin-compatible size composition for glass fibers containing an epoxy film-former, non-ionic

lubricant, cationic lubricant, silane coupling agent and an acid such as acetic or citric acid.

Japanese Patent Application No. 8-325,950 discloses a glass fiber sizing agent including as essential components polyvinyl pyrrolidone, a water-soluble epoxy resin amine addition product and a silane coupling agent which do not require heat removal from finished glass cloth.

Japanese Patent Application No. 7-102,483 discloses a warp secondary sizing agent for glass fiber for weaving glass cloth that does not require heat oil removal. The warp secondary sizing agent is composed mainly of polyvinyl pyrrolidone and contains an additive such as high molecular weight polyethylene oxide. A water-soluble epoxy resin can be included as a binding component.

An inert lubricant for inhibiting abrasion of glass fibers which does not appreciably deteriorate during processing, improves the drilling properties of a laminate incorporating the glass fiber, and which is compatible with polymeric matrix materials is desirable. However, use of inorganic materials has mainly focused on fillers for modifying general physical characteristics of composites rather than improving abrasion-resistance characteristics of reinforcement fibers.

U.S. Patent No. 4,869,954 discloses a sheet-like, thermally conductive material formed of a urethane binder, curing agent and thermally conductive fillers such as aluminum oxide, aluminum nitride, boron nitride, magnesium oxide and zinc oxide and various metals (see col. 2, lines 62-65 and col. 4, lines 3-10). One or more layers of a support material, such as glass fiber cloth, can be included in the thermally conductive material.

U.S. Patent No. 3,312,569 discloses adhering particles of alumina to the surfaces of the glass fibers and Japanese Patent Application No. 9-208,268, as discussed earlier, discloses a cloth having yarn formed from glass fibers coated immediately after spinning with starch or a synthetic resin and inorganic particles such as colloidal silica, calcium carbonate, kaolin and

talc to improve penetration of resin between glass reinforcement fibers during formation of a composite. However the Mohs' hardness values of alumina and silica are greater than about 9 and about 7[1], respectively, which can cause abrasion of softer glass fibers.

U.S. Patent No. 5,541,238 discloses a fiber for reinforcing thermoplastic or thermoset composites which is coated by vapor deposition or plasma process with a single layer of an ultrafine material such as inorganic oxides, nitrides, carbides, borides, metals and combinations thereof having an average particle diameter of 0.005-1 micrometer. Limited space and environmental considerations make the use of vapor deposition or plasma processes under a glass fiber production bushing impractical.

Soviet Union No. 859400 discloses an impregnating composition for manufacturing laminates of glass fiber cloth, the composition containing an alcoholic solution of phenol-formaldehyde resin, graphite, molybdenum disulfide, polyvinyl butyral and surfactant. Volatile alcoholic solvents are not desirable for glass fiber production applications.

U.S. Patent No. 5,217,778 discloses a dry clutch facing including a composite yarn of glass fibers, metallic wire and polyacrylonitrile fibers which are impregnated and coated with a heat curable cement or binder system. The binder can include friction particles such as carbon black, graphite, metal oxides, barium sulfate, aluminum silicate, ground rubber particles, ground organic resins, polymerized cashew nut oil, clay, silica or cryolite (see col. 2, lines 55-66) to modify frictional characteristics of a composite.

There is a need for lubricant coatings for glass fibers which are compatible with a variety of polymeric matrix materials, that reduce drill tip wear and improve the locational accuracy of drilled holes. In addition, it

---

[1] See R. Weast (Ed.), Handbook of Chemistry and Physics, CRC Press (1975) at page F-22 and H. Katz et al. (Ed.), Handbook of Fillers and Plastics, (1987) at page 28, which are hereby incorporated by reference.

would be particularly advantageous if the coating was also compatible with modern air jet weaving equipment to increase productivity.

Summary of the Invention

One aspect of the present invention is a prepreg for an electronic support, the prepreg comprising: (a) a polymeric matrix material; and (b) a fabric comprising a strand comprising glass fibers, at least a portion of the fabric having a coating which is compatible with the polymeric matrix material, the prepreg having a drill tip percent wear of no greater than about 32 percent, as determined after drilling 2000 holes through a stack of 3 laminates, each laminate including eight of the prepregs, at a hole density of 62 holes per square centimeter (400 holes per square inch) and a chip load of 0.001 with a 0.46 mm (0.018 inch) diameter tungsten carbide drill. The present invention also provides a laminate incorporating the prepreg.

Another aspect of the present invention is a prepreg for an electronic support, the prepreg comprising: (a) a polymeric matrix material; and (b) a woven reinforcement fabric comprising a glass fibers, at least a portion of the fabric having a coating which is compatible with the polymeric matrix material, the prepreg having a deviation distance of no greater than about 36 micrometers, as determined after drilling 2000 holes through a stack of 3 laminates at a hole density of 62 holes per square centimeter (400 holes per square inch) and a chip load of 0.001 with a 0.46 mm (0.018 inch) diameter tungsten carbide drill. The present invention also provides a laminate incorporating the prepreg.

Brief Description of the Drawings

The foregoing summary, as well as the following detailed description of the preferred embodiments, will be better understood when read in conjunction with the appended drawings. In the drawings:

Figure 1 is a cross-sectional view of a reinforced laminate according to the present invention;

Figure 2 is a top plan view of one embodiment of a fabric incorporating features of the present invention;

Figure 3 is a perspective view of a coated fiber strand according to the present invention;

Figure 4 is a cross-sectional view of an alternative embodiment of a reinforced laminate according to the present invention;

Figure 5 is a cross-sectional view of an electronic support according to the present invention;

Fig. 6 is a schematic diagram of a method for forming an aperture in a layer of fabric of an electronic support;

Figure 7 is an end view of a drill illustrating the primary cutting edge.

Figure 8 is a schematic of a drill hole pattern.

Detailed Description of the Invention

The laminates of the present invention are reinforced with fabric comprising coated fiber strands, and preferably woven fabric comprising coated glass fiber strands, which can provide the laminate with low coefficient of thermal expansion, good flexural strength, thermal stability, hydrolytic stability, low corrosion and reactivity in the presence of high humidity, reactive acids and alkalies. The coated glass fiber strands are compatible with a variety of polymeric matrix materials, which can eliminate the need for heat or water cleaning of the glass fiber fabric prior to lamination.

Another significant advantage of the laminates of the present invention is that they exhibit improved drillability, i.e. reduced drill tip wear and/or improved drilled hole location accuracy, especially when the laminate is being used as an electronic support. As used herein, "electronic support" means a structure that mechanically supports and/or electrically interconnects elements including but not limited to active electronic components, passive

electronic components, printed circuits, integrated circuits, semiconductor devices and other hardware associated with such elements, such as but not limited to connectors, sockets, retaining clips and heat sinks.

Another advantage of the laminates of the present invention is that they can be fabricated from fiber strands that are suitable for use in an air jet weaving process. As used herein, "air jet weaving" means a type of fabric weaving in which the fill yarn (weft) is inserted into the warp shed by a blast of compressed air from one or more air jet nozzles.

Referring now to the Figures, wherein like numerals indicate like elements throughout, Fig. 1 shows a laminate 10 according to the present invention. The laminate 10 comprises a polymeric matrix material 12 (discussed in detail below) which is reinforced by a reinforcement fabric 14. Fabric 14 can be a woven or nonwoven fabric, such as but not limited to a knit fabric or mat, formed by any suitable knitting, weaving or mat producing process. Preferably the fabric 14 is a woven fabric formed by an air jet weaving process, which is well know to those skilled in the art. The laminate 10 can also be a unidirectional laminate wherein most of the fibers, yarns or strands in each layer of fabric are oriented in the same direction.

Typically, a laminate includes multiple prepregs with each prepreg incorporating fabric 14 and a partially cured polymeric matrix 12, as will be discussed later in more detail. The number of prepregs in a laminate can range from one to about 40. For clarity in the figures, only a single prepreg is shown in the laminate 10.

Referring now to Figs. 2 and 3, the fabric 14 comprises one or more coated fiber strands 16. As used herein, the term "strand" means a plurality of individual fibers. The term "fiber" means an individual filament.

The glass fibers 18 can be formed from any type of fiberizable glass composition known to those skilled in the art, including those prepared from fiberizable glass compositions such as "E-glass", "A-glass", "C-glass", "D-glass", "Q-glass", "R-glass", "S-glass" and E-glass derivatives. As used

herein, the term "fiberizable" means a material capable of being formed into a generally continuous filament, fiber, strand or yarn. As used herein, "E-glass derivatives" means glass compositions that include minor amounts of fluorine and/or boron and preferably are fluorine-free and/or boron-free. Furthermore, as used herein, minor means less than about 1 weight percent fluorine and less than about 5 weight percent boron. Basalt and mineral wool materials are examples of other fiberizable glass materials useful in the present invention. Preferred glass fibers are formed from E-glass or E-glass derivatives. Such compositions are well known to those skilled in the art and further discussion thereof is not believed to be necessary in view of the present disclosure. The glass fibers of the present invention can be formed in any suitable method known in the art, for forming glass fibers. For example, glass fibers can be formed in a direct-melt fiber forming operation or in an indirect, or marble-melt, fiber forming operation. In a direct-melt fiber forming operation, raw materials are combined, melted and homogenized in a glass melting furnace. The molten glass moves from the furnace to a forehearth and into fiber forming apparatus where the molten glass is attenuated into continuous glass fibers. In a marble-melt glass forming operation, pieces or marbles of glass having the final desired glass composition are preformed and fed into a bushing where they are melted and attenuated into continuous glass fibers. If a premelter is used, the marbles are fed first into the premelter, melted, and then the melted glass is fed into a fiber forming apparatus where the glass is attenuated to form continuous fibers. In the present invention, the glass fibers are preferably formed by the direct-melt fiber forming operation. For additional information relating to glass compositions and methods of forming the glass fibers, see K. Loewenstein, <u>The Manufacturing Technology of Glass Fibres</u>, (3d Ed. 1993) at pages 30-44, 47-60, 115-122 and 126-135, U.S. Patents 4,542,106 and 5,789,329, and IPC-EG-140 "Specification for Finished Fabric Woven from 'E' Glass for Printed Boards" at page 1, a publication of The Institute for Interconnecting

and Packaging Electronic Circuits (June 1997), which are hereby incorporated by reference.

The glass fibers can have a nominal filament diameter ranging from about 3.0 to about 35.0 micrometers (corresponding to a filament designation of B through U and above), and preferably have a nominal filament diameter ranging from about 5.0 to about 30.0 micrometers. For fine yarn applications, the average nominal filament diameter preferably in the range of about 5 to about 7 micrometers. The number of fibers per strand can range from about 2 to about 15,000, and is preferably about 100 to about 7000. For further information regarding nominal filament diameters, and designations of glass fibers, see Loewenstein at pages 25 and 27, which are hereby incorporated by reference.

In addition to glass fibers, the coated fiber strand 16 can further comprise fibers 20 formed from other fiberizable inorganic materials, fiberizable organic materials, and mixtures and combinations thereof. The inorganic and organic materials can be either man-made or naturally occurring materials. It will be appreciated by one skilled in the art that the fiberizable inorganic and organic materials can also be polymeric materials. As used herein the term "polymeric material" means a material formed from macromolecules composed of long chains of atoms that are linked together and that can become entangled in solution or in the solid state[2].

Non-limiting examples of suitable non-glass fiberizable inorganic materials include ceramic materials such as silicon carbide, carbon, graphite, mullite, aluminum oxide and piezoelectric ceramic materials. Non-limiting examples of suitable fiberizable organic materials include cotton, cellulose, natural rubber, flax, ramie, hemp, sisal and wool. Non-limiting examples of suitable fiberizable organic polymeric materials include those formed from polyamides (such as nylon and aramids), thermoplastic polyesters (such as

[2] James Mark et al. Inorganic Polymers, Prentice Hall Polymer Science and Engineering Series, (1992) at page 1 which is hereby incorporated by reference.

polyethylene terephthalate and polybutylene terephthalate), acrylics (such as polyacrylonitriles), polyolefins, polyurethanes and vinyl polymers (such as polyvinyl alcohol). Non-glass fiberizable materials useful in the present invention and methods for preparing and processing such fibers are discussed at length in the Encyclopedia of Polymer Science and Technology, Vol. 6 (1967) at pages 505-712, which is hereby incorporated by reference. It is understood that blends or copolymers of any of the above materials and combinations of fibers formed from any of the above materials can be used in the present invention, if desired.

The present invention will now be discussed generally in the context of glass fiber strands, although one skilled in the art would understand that the strand 16 can additionally include one or more of the non-glass fibers discussed above.

Although not limiting in the present invention, in the embodiment of the fabric 14 shown in Fig. 2, at least one and preferably all the fibers 18 of the strand 16 are coated with a layer 22 of a coating composition applied to at least a portion of a surface of the fibers 18 to protect the fiber surface from abrasion during processing and inhibit fiber breakage. Preferably the coating composition is applied to the entire outer surface or periphery of the each of the fibers 18 of the strand 16 as shown in Fig. 3.

The coating composition useful in the present invention are present upon the fibers as a sizing (preferred), a secondary coating applied over a sizing and/or a tertiary or outer coating, as desired. As used herein, the terms "size", "sized" or "sizing" refer to the coating composition applied to the fibers immediately after formation of the fibers. In an alternative embodiment, the terms "size", "sized" or "sizing" additionally refer to the coating composition (also known as a "finishing size") applied to the fibers after at least a portion, and typically all of a conventional primary coating composition has been removed by heat, water or chemical treatment, i.e., a finishing size which is applied to bare glass fibers incorporated into a fabric form. The term

"secondary coating" refers to a coating composition applied secondarily to one or a plurality of strands after a sizing composition is applied, and preferably at least partially dried. This coating can be applied to the fiber before the fiber is incorporated into a fabric or it can be applied to the fiber after the fiber is incorporated into a fabric , e.g. by coating the fabric.

The coating compositions useful in the present invention are preferably aqueous coating compositions. Although not preferred for safety reasons, the coating compositions can contain volatile organic solvents such as alcohol or acetone as needed, but preferably are free of such solvents.

The coating composition useful in the present invention comprises one or more polymeric materials, such as thermosetting materials or thermoplastic materials, which are compatible with the polymeric matrix material 12 of the laminate 10, i.e., the components of the coating composition facilitate wet-out and wet-through of the matrix material upon the fiber strands and provide adequate physical properties in the composite. Preferably the polymeric materials form a generally continuous film when applied to the surface of the fibers 18. The polymeric materials can be water soluble, emulsifiable, dispersible and/or curable. As used herein, the phrase "compatible with the polymeric matrix material" means that the components of the coating composition applied to the glass fibers facilitate wet-through and wet-out of the matrix material upon the fiber strands, provide adequate physical properties in the composite, are chemically compatible with the polymeric matrix material, provide good hydrolytic stability, i.e. resistance to water migration along the fiber surface/matrix material interface, and the coating components (or selected coating components) do not require removal prior to incorporation of the coated fiber into the polymeric matrix material. The measure of the penetration of the polymeric matrix material through a mat or fabric is referred to as "wet-through". The measure of the flowability of the polymeric matrix material through the glass fiber strands to obtain essentially

complete encapsulation of the entire surface of each glass fiber by the polymeric matrix material is referred to as "wet-out".

In one embodiment of the invention, the coating composition applied to fibers 18 that are incorporated into laminate 10 comprises one or more polymeric film forming materials which are compatible with a thermosetting matrix material such as are used to form laminates for printed circuit boards or printed wiring boards (hereinafter individually and collectively referred to as "electronic circuit boards"), for example FR-4 epoxy resins, which are polyfunctional epoxy resins, and in one particular embodiment of the invention, is a difunctional brominated epoxy resins, and polyimides. See 1 Electronic Materials Handbook, ASM International (1989) at pages 534-537, which are hereby incorporated by reference.

Nonlimiting examples of useful polymeric film forming materials include thermoplastic polymeric materials such as thermoplastic polyesters, vinyl polymers, polyolefins, polyamides (e.g. aliphatic polyamides or aromatic polyamides such as aramid), thermoplastic polyurethanes, acrylic polymers and mixtures thereof which are compatible with a thermosetting matrix material. Nonlimiting examples of thermoplastic polyesters include DESMOPHEN 2000 and DESMOPHEN 2001KS, both of which are commercially available from Bayer of Pittsburgh, Pennsylvania, RD-847A polyester resin which is commercially available from Borden Chemicals of Columbus, Ohio, and DYNAKOLL SI 100 resin which is commercially available from Eka Chemicals AB, Sweden. Useful polyamides include the VERSAMID products that are commercially available from General Mills Chemicals, Inc. Useful thermoplastic polyurethanes include WITCOBOND® W-290H that is commercially available from Witco Chemical Corp. of Chicago, Illinois and RUCOTHANE® 2011L polyurethane latex that is commercially available from Ruco Polymer Corp. of Hicksville, New York.

Nonlimiting examples of useful thermosetting polymeric materials include thermosetting polyesters, epoxy materials, vinyl esters, phenolics,

aminoplasts, thermosetting polyurethanes and mixtures thereof which are compatible with a thermosetting matrix material. Suitable thermosetting polyesters can include STYPOL polyesters that are commercially available from Cook Composites and Polymers of Port Washington, Wisconsin and NEOXIL polyesters that are commercially available from DSM B.V. of Como, Italy.

Useful epoxy materials contain at least one epoxy or oxirane group in the molecule, such as polyglycidyl ethers of polyhydric alcohols or thiols. Examples of suitable epoxy polymers include EPON® 826 and EPON® 880 epoxy resins, which are epoxy functional polyglycidyl ethers of bisphenol A commercially available from Shell Chemical Company of Houston, Texas. In one embodiment of a coating composition, the coating composition is essentially free of epoxy materials, i.e., comprises less than about 5 weight percent epoxy materials and more preferably less than about 2 weight percent.

In one nonlimiting embodiment of the coating composition, the coating composition comprise one or more polyesters (e.g. DESMOPHEN 2000 and RD-847A) and one or more additional film-forming polymers selected from the group consisting of vinyl pyrrolidone polymers (preferred), vinyl alcohol polymers and/or starches. Vinyl pyrrolidone polymers useful in the present invention include polyvinyl pyrrolidones such as PVP K-15, PVP K-30, PVP K-60 and PVP K-90, each of which are commercially available from ISP Chemicals of Wayne, New Jersey. Other suitable vinyl polymers include Resyn 2828 and Resyn 1037 vinyl acetate copolymer emulsions, which are commercially available from National Starch and Chemical of Bridgewater, New Jersey. Useful starches include those prepared from potatoes, corn, wheat, waxy maize, sago, rice, milo and mixtures thereof, such as KOLLOTEX 1250 (a low viscosity, low amylose potato-based starch etherified with ethylene oxide) which is commercially available from AVEBE of the Netherlands. The amount of additional polymer is preferably less than about

20 weight percent, and more preferably ranges from about 0.1 to about 5 weight percent. Preferably, the coating composition is essentially free of starch, i.e., contains less than about 5 weight percent starch and more preferably is free of starch, which is often incompatible with the matrix material.

The coating composition can comprise a mixture of one or more thermosetting polymeric materials with one or more thermoplastic polymeric materials. In one embodiment for laminates for electronic circuit boards, the polymeric materials of the coating composition comprise a mixture of RD-847A polyester resin or DYNAKOLL SI 100 resin, PVP K-30 polyvinyl pyrrolidone, DESMOPHEN 2000 polyester and VERSAMID polyamide. In an alternative embodiment suitable for laminates for printed circuit boards, the polymeric materials of the aqueous sizing composition comprise PVP K-30 polyvinyl pyrrolidone, optionally combined EPON 826 epoxy resin.

Generally, the amount of polymeric material can range from about 1 to about 90 weight percent of the coating composition on a total solids basis, preferably about 1 to about 80 weight percent.

In addition to or in lieu of the polymeric materials discussed above, the coating composition preferably comprises one or more coupling agents such as organo silane coupling agents, transition metal coupling agents, phosphonate coupling agents, aluminum coupling agents, amino-containing Werner coupling agents and mixtures thereof. These coupling agents typically have dual functionality. Each metal or silicon atom has attached to it one or more groups which can either react with or compatibilize the fiber surface and/or the components of the polymeric matrix. As used herein, the term “compatibilize” means that the groups are chemically attracted to the fiber surface and/or the components of the coating composition, for example by polar, wetting or solvation forces. In one nonlimiting embodiment, each metal or silicon atom has attached to it one or more hydrolyzable groups that allow the coupling agent to react with the glass fiber surface, and one or more

functional groups that allow the coupling agent to react with components of the polymeric matrix. Examples of hydrolyzable groups include:

$$-OR^1,\quad -O-\overset{\overset{O}{\|}}{C}-R^2,\ -\overset{\overset{H}{|}}{N}-\overset{\overset{O}{\|}}{C}-R^2,\ -O-N=\overset{\overset{R^3}{|}}{C}-R^4,\ -O-N=CR^5,\ \text{and}$$

the monohydroxy and/or cyclic C_2-C_3 residue of a 1,2- or 1,3 glycol, wherein R^1 is C_1-C_3 alkyl; R^2 is H or C_1-C_4 alkyl; R^3 and R^4 are independently selected from H, C_1-C_4 alkyl or C_6-C_8 aryl; and R^5 is C_4-C_7 alkylene. Examples of suitable compatibilizing or functional groups include epoxy, glycidoxy, mercapto, cyano, allyl, alkyl, urethano, halo, isocyanato, ureido, imidazolinyl, vinyl, acrylato, methacrylato, amino or polyamino groups.

Functional organo-silane coupling agents are preferred for use in the present invention. Examples of useful functional organo-silane coupling agents include gamma-aminopropyltrialkoxysilanes, gamma-isocyanatopropyltriethoxysilane, vinyl-trialkoxysilanes, glycidoxypropyltrialkoxysilanes and ureidopropyltrialkoxysilanes. Preferred functional organo silane coupling agents include A-187 gamma-glycidoxypropyltrimethoxysilane, A-174 gamma-methacryloxypropyltrimethoxysilane, A-1100 gamma-aminopropyltriethoxysilane silane coupling agents, A-1108 amino silane coupling agent and A-1160 gamma-ureidopropyltriethoxysilane (each of which are commercially available from OSi Specialties, Inc. of Tarrytown, New York). The organo-silane coupling agent can be at least partially hydrolyzed with water prior to application to the fibers, preferably at about a 1:1 stoichiometric ratio or, if desired, applied in unhydrolyzed form. If desired, the pH of the water can be modified by the addition of an acid or base to initiate or speed the hydrolysis of the coupling agent as is well known in the art.

Suitable transition metal coupling agents include titanium, zirconium, yttrium and chromium coupling agents. Suitable titanate coupling agents and zirconate coupling agents are commercially available from Kenrich

Petrochemical Company. Suitable chromium complexes are commercially available from E.I. duPont de Nemours of Wilmington, Delaware. The amino-containing Werner-type coupling agents are complex compounds in which a trivalent nuclear atom such as chromium is coordinated with an organic acid having amino functionality. Other metal chelate and coordinate type coupling agents known to those skilled in the art also can be used herein.

The amount of coupling agent can range from about 1 to about 30 weight percent of the coating composition on a total solids basis, and preferably about 1 to about 10 weight percent.

Although not limiting in the present invention, in the embodiment of the coating composition shown in Figure 3, the coating composition of the present invention comprises one or more particles 24 that when applied to at least one fiber 18 of strand 16 adheres to the outer surface of the fiber 18 and provides one or more interstitial spaces 30 between adjacent glass fibers 26, 28 of the strand 16. These interstitial spaces 30 correspond generally to the average size 32 of the particles 24 positioned between the adjacent fibers.

The particles 24 of the coating composition are preferably discrete particles. As used herein the term "discrete" means that the particles do not tend to coalesce or combine to form films under processing conditions, but instead generally retain their individual shape or form. In addition, the particles are preferably dimensionally stable. As used herein the term "dimensionally stable particles" means that the particles will generally maintain their average particle size and shape under processing conditions, such as the forces generated between adjacent fibers during weaving, roving and other processing operations, so as to maintain the desired interstitial spaces between adjacent fibers 26, 28. In other words, the particles preferably will not crumble, dissolve or substantially deform in the coating composition to form a particle having a maximum dimension less than its selected average particle size under typical glass fiber processing conditions, such as exposure to temperatures of up to about 25°C and preferably up to

about 100°C, and more preferably up to about 140°C. Additionally, the particles 24 should not substantially enlarge or expand in size under glass fiber processing conditions and, more particularly, under composite processing conditions where the processing temperatures can exceed 150°C. As used herein, the phrase "should not substantially enlarge in size" in reference to the particles means that the particles should not expand or increase in size to more than approximately 3 times their initial size during processing. Preferably, the coating compositions of the present invention are essentially free of heat expandable hollow particles. As used herein, the term "heat expandable hollow particles" means hollow particles filled with or containing a blowing agent, which when exposed to temperatures sufficient to volatilize the blowing agent expand or substantially enlarge in size. As used herein the term "essentially free of" means the sizing composition comprises less than about 20 weight percent of heat expandable hollow particles on a total solids basis, more preferably less than about 5 weight percent, and most preferably less than 0.001 weight percent. Furthermore, as used herein, the term "dimensionally stable" includes both crystalline and non-crystalline materials.

In addition, although not required, it is preferred that the particles 24 are non-waxy. The term "non-waxy" means the materials from which the particles are formed are not wax-like. As used herein, the term "wax-like" means materials composed primarily of unentangled hydrocarbons chains having an average carbon chain length ranging from about 25 to about 100 carbon atoms[3,4].

Preferably, the particles 24 in the coating composition are discrete, dimensionally stable, non-waxy particles. In a specific, nonlimiting

---

[3] L. H. Sperling Introduction of Physical Polymer Science, John Wiley and Sons, Inc. (1986) at pages 2-5, which are hereby incorporated by reference.

[4] W. Pushaw, et al. "Use of Micronised Waxes and Wax Dispersions in Waterborne Systems" Polymers, Paint, Colours Journal, V.189, No. 4412 January 1999 at pages 18-21 which are hereby incorporated by reference.

embodiment of the present invention, the average particle size 32 of the particles 24 is at least about 0.1 micrometers, preferably at least about 0.5 micrometers, and ranges from about 0.1 micrometers to about 5 micrometers and preferably from about 0.5 micrometers to about 3.0 micrometers. In one embodiment, the particles 24 are at least about 1 micrometer and preferably in the range of about 1 to about 3 micrometers. In this nonlimiting embodiment, the particles 24 have an average particle sizes 32 that is generally smaller than the average diameter of the fibers 18 to which the coating composition is applied. It has been observed that twisted yarns made from fiber strands 16 having a layer 22 of a residue of a primary sizing composition comprising particles 24 having average particles sizes 32 discussed above can provide sufficient spacing between adjacent fibers 26, 28 to permit air-jet weavability (i.e. air-jet transport across the loom) while maintaining the integrity of the fiber strand 16 and providing acceptable "wet-through" and "wet-out" characteristics when impregnated with a polymeric matrix material.

In another specific, non-limiting embodiment of the present invention the average particles size 32 of particles 24 is at least 3 micrometers, preferably at least about 5 micrometers, and ranges from 3 to about 1000 micrometers, preferably about 5 to about 1000 micrometers, and more preferably about 10 to about 25 micrometers. Preferably, each of the particles 24 has a minimum particle size of at least 3 micrometers, and preferably of at least about 5 micrometers. It is also preferred in this embodiment that the average particle size 32 of the particles 24 corresponds generally to the average nominal diameter of the glass fibers. It has been observed that fabrics made with strands coated with the particles of the sizes as discussed above exhibit good "wet-through" and "wet-out" characteristics when impregnated with a polymeric matrix material.

It will be recognized by one skilled in the art that mixtures of one or more particles 24 having different average particle sizes 32 can be

incorporated into the sizing composition in accordance with the present invention to impart the desired properties and processing characteristics to the fiber strands 16 and to the products subsequently made therefrom. More specifically, different sized particles can be combined in required amounts so as to provide fibers having good air-jet transport properties as well a fabric exhibiting good wet-out and wet-through characteristics.

Although not limiting in the present invention, the configuration or shape of the particles 24 can be generally spherical (such as beads, microbeads or solid hollow spheres), cubic, platy or acicular (elongated or fibrous), as desired. In addition, the particles 24 can have a structure that is hollow, porous, or void free, or a combination thereof. In addition, the particles 24 can have a combination of these structures, e.g. a hollow center with porous or solid walls. For more information on suitable particle characteristics, see H. Katz et al. (Ed.), Handbook of Fillers and Plastics (1987) at pages 9-10, which are hereby incorporated by reference.

Glass fibers are subject to abrasive wear by contact with asperities of adjacent glass fibers and/or other solid objects or materials which the glass fibers contact during forming and subsequent processing, such as weaving or roving. "Abrasive wear", as used herein, means scraping or cutting off of bits of the glass fiber surface or breakage of glass fibers by frictional contact with particles, edges or entities of materials which are hard enough to produce damage to the glass fibers. See K. Ludema, Friction, Wear, Lubrication, (1996) at page 129, which is hereby incorporated by reference. Abrasive wear of glass fiber strands causes strand breakage during processing and surface defects in products such as woven cloth and composites, which increases waste and manufacturing cost.

To minimize abrasive wear, the particles 24 have a hardness value which does not exceed, i.e., is less than or equal to, a hardness value of the glass fiber(s). The hardness values of the particles and glass fibers can be determined by any conventional hardness measurement method, such as

Vickers or Brinell hardness, but is preferably determined according to the original Mohs' hardness scale which indicates the relative scratch resistance of the surface of a material. The Mohs' hardness value of glass fibers generally ranges from about 4.5 to about 6.5, and is preferably about 6. See R. Weast (Ed.), Handbook of Chemistry and Physics, CRC Press (1975) at page F-22, which is hereby incorporated by reference. The Mohs' hardness value of the particles suitable for use in the coating composition discussed above preferably ranges from about 0.5 to about 6. The Mohs' hardness values of several non-limiting examples of particles suitable for use in the present invention are given in Table A below.

Table A

Particle material	Mohs' hardness (original scale)
boron nitride	about 2[5]
graphite	about 0.5-1[6]
molybdenum disulfide	about 1[7]
talc	about 1-1.5[8]
mica	about 2.8-3.2[9]
kaolinite	about 2.0-2.5[10]
gypsum	about 1.6-2[11]
calcite (calcium carbonate)	about 3[12]
calcium fluoride	about 4[13]
zinc oxide	about 4.5[14]
aluminum	about 2.5[15]
copper	about 2.5-3[16]
iron	about 4-5[17]
gold	about 2.5-3[18]
nickel	about 5[19]
palladium	about 4.8[20]
platinum	about 4.3[21]
silver	about 2.5-4[22]

As mentioned above, the Mohs' hardness scale relates to the resistance of a material to scratching. The instant invention therefore further contemplates particles that have a hardness at their surface that is different from the hardness of the internal portions of the particle beneath its surface. More specifically, the surface of the particle can be modified in any manner

5 K. Ludema, Friction, Wear, Lubrication, (1996) at page 27, which is hereby incorporated by reference.
6 R. Weast (Ed.), Handbook of Chemistry and Physics, CRC Press (1975) at page F-22.
7 R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 793, which is hereby incorporated by reference.
8 Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 1113, which is hereby incorporated by reference.
9 Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 784, which is hereby incorporated by reference.
10 Handbook of Chemistry and Physics at page F-22.
11 Handbook of Chemistry and Physics at page F-22.
12 Friction, Wear, Lubrication at page 27.
13 Friction, Wear, Lubrication at page 27.
14 Friction, Wear, Lubrication at page 27.
15 Friction, Wear, Lubrication at page 27.
16 Handbook of Chemistry and Physics at page F-22.
17 Handbook of Chemistry and Physics at page F-22.
18 Handbook of Chemistry and Physics at page F-22.
19 Handbook of Chemistry and Physics at page F-22.
20 Handbook of Chemistry and Physics at page F-22.
21 Handbook of Chemistry and Physics at page F-22.
22 Handbook of Chemistry and Physics at page F-22.

well known in the art, including but not limited to chemically changing its surface characteristics using techniques known in the art, such that the surface hardness of the particle is not greater than the hardness of the glass fibers while the hardness of the particle beneath the surface is greater than the hardness of the glass fibers. As another alternative, a particle can be coated, clad or encapsulated to form a composite particle (as discussed later) that has a softer surface.

Generally, particles 24 useful in the present invention can be formed from materials selected from the group consisting of polymeric and non-polymeric inorganic materials, polymeric and non-polymeric organic materials, composite materials and mixtures thereof. As used herein the term "polymeric inorganic material" means a polymeric material having a backbone repeat unit based on an element or elements other than carbon. For more information see J. E. Mark et al. at page 5 which is hereby incorporated by reference. Polymeric organic materials include synthetic polymeric materials, semisynthetic polymeric materials and natural polymeric materials. An "organic material", as used herein, means all compounds of carbon except such binary compounds as the carbon oxides, the carbides, carbon disulfide, etc.; such ternary compounds as the metallic cyanides, metallic carbonyls, phosgene, carbonyl sulfide, etc.; and metallic carbonates, such as calcium carbonate and sodium carbonate. See R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at pages 761-762 which are hereby incorporated by reference. More generally, organic materials include carbon containing compounds wherein the carbon is typically bonded to itself and to hydrogen, and often to other elements as well and excludes carbon-containing ionic compounds. See M. Silberberg, Chemistry The Molecular Nature of Matter and Change, (1996) at page 586, which is hereby incorporated by reference. The term " inorganic material" generally means all materials that are not compounds of carbon with the exception of carbon oxides and carbon disulfide. See R. Lewis, Sr., Hawley's Condensed

Chemical Dictionary, (12th Ed. 1993) at page 636 which are hereby incorporated by reference. As used herein the term "inorganic materials" means any material that is not an organic material. As used here in the term "composite material" means a combination of two or more different materials. For more information on particles useful in the present invention, see G. Wypych, Handbook of Fillers, 2nd Ed. (1999) at pages 15-202, which are hereby incorporated by reference.

Non-polymeric inorganic materials useful in forming the particles 24 include ceramic materials and metallic materials. Suitable ceramic materials include metal nitrides, metal oxides, metal carbides, metal sulfides, metal borides, metal silicates, metal carbonates and mixtures thereof.

A non-limiting example of a suitable metal nitride is boron nitride, which is the preferred inorganic material from which particles useful in the present invention are formed. A non-limiting example of a useful metal oxide is zinc oxide. Suitable metal sulfides include molybdenum disulfide, tantalum disulfide, tungsten disulfide and zinc sulfide. Useful metal silicates include aluminum silicates and magnesium silicates, such as vermiculite. Suitable metallic materials include graphite, molybdenum, platinum, palladium, nickel, aluminum, copper, gold, iron, silver and mixtures thereof.

Although not required, preferably the particles 24 are also solid lubricants. As used herein, "solid lubricant" means any solid used between two surfaces to provide protection from damage during relative movement and/or to reduce friction and wear. More preferably, the particles 24 are an inorganic solid lubricant. As used herein, "inorganic solid lubricant" means that the inorganic particles 24 have a characteristic crystalline habit which causes them to shear into thin, flat plates which readily slide over one another and thus produce an antifriction lubricating effect between the glass fiber surface and an adjacent solid surface, at least one of which is in motion. (See R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 712, which is hereby incorporated by reference.) Friction is the

resistance to sliding one solid over another. See F. Clauss, Solid Lubricants and Self-Lubricating Solids, (1972) at page 1, which is hereby incorporated by reference.

In one particular embodiment useful in the present invention, the solid lubricant particles have a lamellar structure which is believed to contribute to reduced tool wear when drilling holes through the laminae, as will discussed later in more detail. Particles having a lamellar structure are composed of sheets or plates of atoms in hexagonal array, with strong bonding within the sheet and weak van der Waals bonding between sheets, providing low shear strength between sheets. A non-limiting example of a lamellar structure is a hexagonal crystal structure. See Friction, Wear, Lubrication at page 125, Solid Lubricants and Self-Lubricating Solids at pages 19-22, 42-54, 75-77, 80-81, 82, 90-102, 113-120 and 128, and W. Campbell "Solid Lubricants", Boundary Lubrication; An Appraisal of World Literature, ASME Research Committee on Lubrication (1969) at pages 202-203, which are hereby incorporated by reference. Inorganic particles having a lamellar fullerene (buckyball) structure are also useful in the present invention.

Non-limiting examples of suitable inorganic solid lubricant particles having a lamellar structure include boron nitride, graphite, metal dichalcogenides, mica, talc, gypsum, kaolinite, calcite, cadmium iodide, silver sulfide and mixtures thereof. Preferred inorganic solid lubricant particles include boron nitride, graphite, metal dichalcogenides and mixtures thereof. Suitable metal dichalcogenides include molybdenum disulfide, molybdenum diselenide, tantalum disulfide, tantalum diselenide, tungsten disulfide, tungsten diselenide and mixtures thereof.

A non-limiting example of an inorganic solid lubricant material for use in the coating composition of the present invention having a hexagonal crystal structure is boron nitride. Particles formed from boron nitride, zinc sulfide and montmorillonite also provide good whiteness in composites with polymeric matrix materials such as nylon 6,6.

Non-limiting examples of boron nitride particles suitable for use in the present invention are PolarTherm® 100 Series (PT 120, PT 140, PT 160 and PT 180), 300 Series (PT 350) and 600 Series (PT 620, PT 630, PT 640 and PT 670) boron nitride powder particles which are commercially available from Advanced Ceramics Corporation of Lakewood, Ohio. "PolarTherm® Thermally Conductive Fillers for Polymeric Materials", a technical bulletin of Advanced Ceramics Corporation of Lakewood, Ohio (1996), is hereby incorporated by reference. These particles have a thermal conductivity of about 250-300 Watts per meter °K at 25°C, a dielectric constant of about 3.9 and a volume resistivity of about 10^{15} ohm-centimeters. The 100 Series powder particles have an average particle size ranging from about 5 to about 14 micrometers, the 300 Series particles have an average particle size ranging from about 100 to about 150 micrometers and the 600 Series particles have an average particle size ranging from about 16 to greater than about 200 micrometers.

The particles 24 can be formed from non-polymeric, organic materials. Examples of non-polymeric, organic materials useful in the present invention include but are not limited to stearates (such as zinc stearate and aluminum stearate), carbon black and stearamide.

The particles 24 can be formed from inorganic polymeric materials. Non-limiting examples of useful inorganic polymeric materials include polyphosphazenes, polysilanes, polysiloxane, polygeremanes, polymeric sulfur, polymeric selenium, silicones and mixtures thereof. A specific, non-limiting example of a particle formed from an inorganic polymeric material suitable for use in the present invention is Tospearl[23], which is a particle formed from cross-linked siloxanes and is commercially available from Toshiba Silicones Company, Ltd. of Japan.

---

[23] See R. J. Perry "Applications for Cross-Linked Siloxane Particles" Chemtech, February 1999 at pages 39-44.

Suitable synthetic, organic polymeric materials from which the particles can be formed include, but are not limited to, thermosetting materials and thermoplastic materials. Suitable thermosetting materials include thermosetting polyesters, vinyl esters, epoxy materials, phenolics, aminoplasts, thermosetting polyurethanes and mixtures thereof. A specific, non-limiting example of a preferred synthetic polymeric particle formed from an epoxy material is an epoxy microgel particle.

Suitable thermoplastic materials include thermoplastic polyesters, polycarbonates, polyolefins, acrylic polymers, polyamides, thermoplastic polyurethanes, vinyl polymers and mixtures thereof. Preferred thermoplastic polyesters include but are not limited to polyethylene terephthalate, polybutylene terephthalate and polyethylene naphthalate. Preferred polyolefins include but are not limited to polyethylene, polypropylene and polyisobutene. Preferred acrylic polymers include copolymers of styrene and acrylic and polymers containing methacrylate. Non-limiting examples of synthetic polymeric particles formed from an acrylic copolymer are ROPAQUE® HP-1055[24], which is an opaque, non-film-forming, styrene acrylic polymeric synthetic pigment having a 1.0 micrometer particle size, a solids content of 26.5 percent by weight and a 55 percent void volume, ROPAQUE® OP-96[25], which is an opaque, non-film-forming, styrene acrylic polymeric synthetic pigment dispersion having a particle size of 0.55 micrometers and a solids content of 30.5 percent by weight, and ROPAQUE® OP-62 LO[26] which is also an opaque, non-film-forming, styrene acrylic polymeric synthetic pigment dispersion having a particles size of 0.40 micrometers and a solids

---

[24] See product property sheet entitled: "ROPAQUE® HP-1055, Hollow Sphere Pigment for Paper and Paperboard Coatings" October 1994, available from Rohm and Haas Company, Philadelphia, PA at page 1 which is hereby incorporated by reference.

[25] See product technical bulletin entitled: "Architectural Coatings- ROPAQUE® OP-96, The All Purpose Pigment", April 1997 available from Rohm and Haas Company, Philadelphia, PA at page 1 which is hereby incorporated by reference.

[26] Ibid.

content of about 36.5 percent by weight, each of which are commercially available from Rohm and Haas Company of Philadelphia, Pennsylvania.

Suitable semisynthetic, organic polymeric materials from which the particles 24 can be formed include but are not limited to cellulosics, such as methylcellulose and cellulose acetate; and modified starches, such as starch acetate and starch hydroxyethyl ethers.

Suitable natural polymeric materials from which the particles 24 can be formed include but are not limited to polysaccharides, such as starch; polypeptides, such as casein; and natural hydrocarbons, such as natural rubber and gutta percha.

In one embodiment of the present invention, the polymeric particles 18 are formed from hydrophobic polymeric materials to reduce or limit moisture absorption by the coated strand. Non-limiting examples of hydrophobic polymeric materials believed to be useful in the present invention include but are not limited to polyethylene, polypropylene, polystyrene and polymethylmethacrylate. Non-limiting examples of polystyrene copolymers include ROPAQUE® HP-1055, ROPAQUE® OP-96, and ROPAQUE® OP-62 LO pigments (each discussed above).

In another embodiment of the present invention, polymeric particles 18 are formed from polymeric materials having a glass transition temperature (T_g) and/or melting point greater than about 25°C and preferably greater than about 50°C.

Composite particles 24 useful in the present invention include particles formed by cladding, encapsulating or coating particles formed from a primary material with one or more secondary materials. For example, an inorganic particle formed from an inorganic material such as silicon carbide or aluminum nitride can be provided with a silica, carbonate or nanoclay coating to form a useful composite particle. In another example, a silane coupling agent with alkyl side chains can be reacted with the surface of an inorganic particle formed from an inorganic oxide to provide a useful composite particle

having a "softer" surface. Other examples include cladding, encapsulating or coating particles formed from organic or polymeric materials with inorganic materials or different organic or polymeric materials. A specific non-limiting example of such composite particles is DUALITE, which are synthetic polymeric particles coated with calcium carbonate that is commercially available from Pierce and Sevens Corporation of Buffalo, New York.

In still another embodiment of the present invention, the particles 24 can be hollow particles formed from materials selected from the group consisting of inorganic materials, organic materials, polymeric materials, composite materials and mixtures thereof. Non-limiting examples of suitable materials from which the hollow particles can be formed are described above. Non-limiting examples of a hollow polymeric particle useful in present invention are ROPAQUE® HP-1055, ROPAQUE® OP-96 and ROPAQUE® OP-62 LO pigments (each discussed above). For other non-limiting examples of hollow particles that can be useful in the present invention see H. Katz et al. (Ed.) (1987) at pages 437-452 which are hereby incorporated by reference.

The solid lubricant particles 24 can be present in a dispersion, suspension or emulsion in water. Other solvents, such as mineral oil or alcohol (preferably less than about 5 weight percent), can be included in the sizing composition, if desired. A non-limiting example of a preferred dispersion of about 25 weight percent boron nitride particles in water is ORPAC BORON NITRIDE RELEASECOAT-CONC which is commercially available from ZYP Coatings, Inc. of Oak Ridge, Tennessee. "ORPAC BORON NITRIDE RELEASECOAT-CONC", a technical bulletin of ZYP Coatings, Inc., is hereby incorporated by reference. The boron nitride particles in this product have an average particle size of less than about 3 micrometers and include about 1 percent of magnesium-aluminum silicate to bind the boron nitride particles to the substrate to which the dispersion is applied. Other useful products which are commercially available from ZYP

Coatings include BORON NITRIDE LUBRICOAT® paint, BRAZE STOP and WELD RELEASE products. Specific, non-limiting examples of emulsions and dispersions of synthetic polymeric particles formed from acrylic polymers and copolymers include: Rhoplex® GL-623[27] which is an all acrylic firm polymer emulsion having a solids content of 45 percent by weight and a glass transition temperature of about 98°C; EMULSION E-2321[28] which is a hard, methacrylate polymer emulsion having a solids content of 45 percent by weight and a glass transition temperature of about 105°C; ROPAQUE® OP-96 (discussed above), which is supplied as a dispersion having a particle size of 0.55 micrometers and a solids content of 30.5 percent by weight; ROPAQUE® OP-62 LO (discussed above), which is also a opaque, non-film-forming synthetic pigment dispersion having a particles size of 0.40 micrometers and a solids content of about 36.5 percent by weight; and ROPAQUE® HP-1055 (discussed above), which is supplied as a dispersion having a solids content of about 26.5 percent by weight; all of which are commercially available from Rohm and Haas Company of Philadelphia, Pennsylvania.

Although not required, it is preferred that the particles 24 be non-hydratable, inorganic solid lubricant particles. As used herein, "non-hydratable" means that the solid inorganic lubricant particles do not react with molecules of water to form hydrates and do not contain water of hydration or water of crystallization. A "hydrate" is produced by the reaction of molecules of water with a substance in which the H-OH bond is not split. See R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at pages 609-610 and T. Perros, Chemistry, (1967) at pages 186-187, which are hereby incorporated by reference. Structurally, hydratable inorganic materials

---

[27] See product property sheet entitled: "Rhoplex® GL-623, Self-Crosslinking Acrylic Binder of Industrial Nonwovens", March 1997 available from Rohm and Haas Company, Philadelphia, PA which is hereby incorporated by reference.

include at least one hydroxyl group within a layer of a crystal lattice (but not including hydroxyl groups in the surface planes of a unit structure or materials which absorb water on their surface planes or by capillary action), for example as shown in the structure of kaolinite given in Fig. 3.8 at page 34 of J. Mitchell, Fundamentals of Soil Behavior (1976) and as shown in the structure of 1:1 and 2:1 layer minerals shown in Figs. 18 and 19, respectively, of H. van Olphen, Clay Colloid Chemistry, (2d Ed. 1977) at page 62, which are hereby incorporated by reference. A "layer" of a crystal lattice is a combination of sheets, which is a combination of planes of atoms. See Minerals in Soil Environments, Soil Science Society of America (1977) at page 196-199, which is hereby incorporated by reference. The assemblage of a layer and interlayer material (such as cations) is referred to as a unit structure.

Hydrates contain coordinated water, which coordinates the cations in the hydrated material and cannot be removed without the breakdown of the structure, and/or structural water, which occupies interstices in the structure to add to the electrostatic energy without upsetting the balance of charge. See R. Evans, An Introduction to Crystal Chemistry, (1948) at page 276, which is hereby incorporated by reference.

While not preferred, the aqueous sizing composition can contain hydratable or hydrated inorganic solid lubricant materials in addition to the non-hydratable inorganic solid lubricant materials discussed above. Non-limiting examples of such hydratable inorganic solid lubricant materials are clay mineral phyllosilicates, including micas (such as muscovite), talc, montmorillonite, kaolinite and gypsum.

Preferably, the coating composition is essentially free of hydratable inorganic solid lubricant particles or abrasive silica particles or calcium

---

[28] See product property sheet entitled: "Building Products Industrial Coatings- Emulsion E-2321", 1990, available from Rohm and Haas Company, Philadelphia, PA which is hereby incorporated by reference.

carbonate, i.e., comprises less than about 20 weight percent of hydratable inorganic lubricant particles, abrasive silica particles or calcium carbonate on a total solids basis, more preferably less than about 5 weight percent, and most preferably less than 0.001 weight percent.

In an alternative embodiment useful in the present invention, the particles 24 are formed from organic polymeric materials selected from the group consisting of thermosetting materials, thermoplastic materials, starches and mixtures thereof. Suitable thermosetting materials include thermosetting polyesters, vinyl esters, epoxy materials, phenolics, aminoplasts, thermosetting polyurethanes and mixtures thereof, such as are discussed below. Suitable thermoplastic materials include vinyl polymers, thermoplastic polyesters, polyolefins, polyamides, thermoplastic polyurethanes, acrylic polymers and mixtures thereof. Preferred organic particles are in the form of microbeads or hollow spheres.

Although not required, in one embodiment useful in the present invention, the particles 24 are thermally conductive, i.e., have a thermal conductivity greater than about 30 Watts per meter K, and preferably is greater than about 100 Watts per meter K, and more preferably ranges from about 100 to about 2000 Watts per meter K. As used herein, "thermal conductivity" means the property of the particle 24 that describes its ability to transfer heat through itself. See R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 305, which is hereby incorporated by reference.

The thermal conductivity of a solid material can be determined by any method known to one skilled in the art. For example, if the thermal conductivity of the material to be tested ranges from about 0.001 Watts per meter K to about 100 Watts per meter K, the thermal conductivity of the material can be determined using the preferred guarded hot plate method according to ASTM C-177-85 (which is hereby incorporated by reference) at a temperature of about 300K. If the thermal conductivity of the material to be

tested ranges from about 20 Watts per meter K to about 1200 Watts per meter K, the thermal conductivity of the material can be determined using the guarded hot flux sensor method according to ASTM C-518-91 (which is hereby incorporated by reference). It is believed that the materials with higher thermal conductivity will more quickly dissipate the heat generated during a drilling operation from the hole area, resulting in prolonged drill tip life. The thermal conductivity of selected material in Table A is included in Table B.

Although not required, in another embodiment useful in the present invention, the particles 24 are electrically insulative or have high electrical resistivity, i.e., have an electrical resistivity greater than about 1000 microohm-cm. Use of particles having high electrical resistivity is preferred for conventional electronic circuit board applications to inhibit loss of electrical signals due to conduction of electrons through the reinforcement. For specialty applications, such as circuit boards for microwave, radio frequency interference and electromagnetic interference applications, particles having high electrical resistivity are not required. The electrical resistance of selected materials in Table A is included in Table B.

It will be appreciated by one skilled in the art that particles 24 of the coating composition can include any combination or mixture of particles 24 discussed above. More specifically, the particles 24 can include additional particles made from any of the materials described above for forming the particles 24.

The solid lubricant particles, if present, can comprise about 1 to about 1 weight percent of the coating composition on a total solids basis, preferably about 1 to about 60 weight percent. In one embodiment, the coating composition can contain about 2 to about 10 weight percent boron nitride on total solids basis. In another embodiment of the invention wherein a combination of different particles are used, the coating composition contains about 20 to about 60 weight percent of particles 24 on total solids basis, and

preferably about 35 to about 55 weight percent, and more preferably about 30 to about 50 weight percent.

The coating composition can further comprise one or more softening agents, or surfactants, that impart a uniform charge to the surface of the fibers, causing the fibers to repel from each other and reducing the friction between the fibers, so as to function as a lubricant. Although not required, it is preferred that the softening agents are chemically different from the polymeric materials discussed above. While the coating composition can comprise up to about 60 weight percent softening agent, preferably the coating composition is essentially free of softening agents, i.e., contains less than about 10 weight percent softening agent, and more preferably contains less than about 5 weight percent softening agent. Examples of such softening agents include cationic, non-ionic or anionic softening agents and mixtures thereof, such as amine salts of fatty acids, alkyl imidazoline derivatives such as CATION X, which is commercially available from Rhone Poulenc of Princeton, New Jersey, acid solubilized fatty acid amides, condensates of a fatty acid and polyethylene imine and amide substituted polyethylene imines, such as EMERY® 6717, a partially amidated polyethylene imine commercially available from Henkel Corporation of Kankakee, Illinois. For more information on softening agents, see A. J. Hall, Textile Finishing, 2nd Ed. (1957) at pages 108-115, which are hereby incorporated by reference.

The coating composition can include one or more emulsifying agents for emulsifying or dispersing components of the coating composition, such as the organic and inorganic particles. Non-limiting examples of suitable emulsifying agents or surfactants include polyoxyalkylene block copolymers (such as PLURONIC™ F-108 polyoxypropylene-polyoxyethylene copolymer which is commercially available from BASF Corporation of Parsippany, New Jersey), ethoxylated alkyl phenols (such as IGEPAL CA-630 ethoxylated octylphenoxyethanol which is commercially available from GAF Corporation of

Wayne, New Jersey), polyoxyethylene octylphenyl glycol ethers, ethylene oxide derivatives of sorbitol esters, polyoxyethylated vegetable oils (such as ALKAMULS EL-719, which is commercially available from Rhone-Poulenc) and nonylphenol surfactants (such as MACOL NP-6 which is commercially available from BASF of Parsippany, New Jersey). Generally, the amount of emulsifying agent can range from about 1 to about 30 weight percent of the coating composition on a total solids basis.

The coating composition can further include one or more lubricious materials that are chemically different from the polymeric materials and softening agents discussed above to impart desirable processing characteristics to the fiber strands during weaving. Suitable lubricious materials can be selected from the group consisting of oils, waxes, greases and mixtures thereof. Non-limiting examples of wax materials useful in the present invention include aqueous soluble, emulsifiable or dispersible wax materials such as vegetable, animal, mineral, synthetic or petroleum waxes, e.g. paraffin. Oils useful in the present invention include both natural oils, semisynthetic oils and synthetic oils. Generally, the amount of wax or other lubricious material can range from 0 to about 80 weight percent of the sizing composition on a total solids basis, preferably from about 1 to about 50 weight percent, more preferably from about 20 to about 40 weight percent, and most preferably from about 25 to about 35 weight percent.

Preferred lubricious materials include waxes and oils having polar characteristics, and more preferably include highly crystalline waxes having polar characteristics and melting points above about 35°C and more preferably above about 45°C. Such materials are believed to improve the wet-out and wet-through of polar resins on fiber strands coated with sizing compositions containing such polar materials as compared to fiber strands coated with sizing compositions containing waxes and oils that do not have polar characteristics. Preferred lubricious materials having polar characteristics include esters formed from reacting (1) a monocarboxylic acid

and (2) a monohydric alcohol. Non-limiting examples of such fatty acid esters useful in the present invention include cetyl palmitate, which is preferred (such as is available from Stepan Company of Maywood, New Jersey as KESSCO 653 or STEPANTEX 653), cetyl myristate (also available from Stepan Company as STEPANLUBE 654), cetyl laurate, octadecyl laurate, octadecyl myristate, octadecyl palmitate and octadecyl stearate. Other fatty acid ester, lubricious materials useful in the present invention include trimethylolpropane tripelargonate, natural spermaceti and triglyceride oils, such as but not limited to soybean oil, linseed oil, epoxidized soybean oil, and epoxidized linseed oil.

While not preferred, the coating composition can include one or more other lubricious materials, such as non-polar petroleum waxes, in lieu of or in addition to of those lubricious materials discussed above. Non-limiting examples of non-polar petroleum waxes include MICHEM® LUBE 296 microcrystalline wax, POLYMEKON® SPP-W microcrystalline wax and PETROLITE 75 microcrystalline wax which are commercially available from Michelman Inc. of Cincinnati, Ohio and the Petrolite Corporation of Tulsa, Oklahoma, respectively.

Although not required, if desired the coating composition can also include a resin reactive diluent to further improve lubrication of the coated fiber strands of the present invention and provide good processibility in weaving and knitting by reducing the potential for fuzz, halos and broken filaments during such manufacturing operations, while maintaining resin compatibility. As used herein, "resin reactive diluent" means that the diluent includes functional groups that are capable of chemically reacting with the same resin with which the coating composition is compatible. The diluent can be any lubricant with one or more functional groups that react with a resin system, preferably functional groups that react with an epoxy resin system, and more preferably functional groups that react with an FR-4 epoxy resin system. Non-limiting examples of suitable lubricants

include lubricants with amine groups, alcohol groups, anhydride groups, acid groups or epoxy groups. A non-limiting example of a lubricant with an amine group is a modified polyethylene amine, e.g. EMERY 6717, which is a partially amidated polyethylene imine commercially available from Henkel Corporation of Kankakee, Illinois. A non-limiting example of a lubricant with an alcohol group is polyethylene glycol, e.g. CARBOWAX 300, which is a polyethylene glycol that is commercially available from Union Carbide of Danbury, Connecticut. A non-limiting example of a lubricant with an acid group is fatty acids, e.g. stearic acid and salts of stearic acids. Non-limiting examples of lubricants with an epoxy group include epoxidized soybean oil and epoxidized linseed oil, e.g. FLEXOL LOE, which is an epoxidized linseed oil, and FLEXOL EPO, which is an epoxidized soybean oil, both commercially available from Union Carbide of Danbury, Connecticut, and LE-9300 epoxidized silicone emulsion, which is commercially available from Witco Corporation OSi Specialties, Inc. of Danbury, Connecticut. Although not limiting in the present invention, the sizing composition can include a resin reactive diluent as discussed above in an amount up to about 15 weight percent of the sizing composition on a total solids basis.

Crosslinking materials, such as melamine formaldehyde, and plasticizers, such as phthalates, trimellitates and adipates, can also be included in the coating composition. The amount of crosslinker or plasticizer can range from about 1 to about 5 weight percent of the coating composition on a total solids basis.

Other additives can be included in the coating composition, such as silicones, fungicides, bactericides and anti-foaming materials, generally in an amount of less than about 5 weight percent. Organic and/or inorganic acids or bases in an amount sufficient to provide the coating composition with a pH of about 2 to about 10 can also be included. A non-limiting example of a suitable silicone emulsion is LE-9300 epoxidized silicone emulsion that is

commercially available from OSi Specialties, Inc. of Danbury, Connecticut. An example of a suitable bactericide is BIOMET 66 antimicrobial compound, which is commercially available from M & T Chemicals of Rahway, New Jersey. Suitable anti-foaming materials are the SAG materials, which are commercially available from OSi Specialties, Inc. of Danbury, Connecticut and MAZU DF-136, which is available from BASF Company of Parsippany, New Jersey. Ammonium hydroxide can be added to the coating composition for stabilization, if desired. Water (preferably deionized) is preferably included in the coating composition in an amount sufficient to facilitate application of a generally uniform coating upon the strand, generally in an amount of about 25 to about 99 weight percent. The weight percentage of solids of an aqueous coating composition generally ranges from about 1 to about 75 weight percent.

The coating composition is preferably essentially free of glass materials. As used herein, "essentially free of glass materials" means that the coating composition comprises less than 20 volume percent of glass matrix materials for forming glass composites, preferably less than about 5 volume percent, and more preferably is free of glass materials. Examples of such glass matrix materials include black glass ceramic matrix materials or aluminosilicate matrix materials such as are well known to those skilled in the art.

In one nonlimiting embodiment of a fabric for electronic circuit boards of the present invention, the glass fibers of the coated fiber strands have applied thereto a primary layer of a dried residue of an aqueous sizing composition comprising PolarTherm® 160 boron nitride powder and/or ORPAC BORON NITRIDE RELEASECOAT-CONC dispersion, PVP K-30 polyvinyl pyrrolidone, A-174 acrylic-functional organo silane coupling agent, A-187 epoxy-functional organo silane coupling agent, ALKAMULS EL-719 polyoxyethylated vegetable oil, EMERY® 6717 partially amidated polyethylene imine, RD-847A polyester, DESMOPHEN 2000 polyester,

PLURONICS F-108 polyoxypropylene-polyoxyethylene copolymer, ICONOL NP-6 alkoxylated nonyl phenol and SAG 10 antifoaming material.

In another embodiment of fabric for electronic circuit boards of the present invention, glass fibers of the coated fiber strands of the present invention have applied thereto a primary layer of a dried residue of an aqueous sizing composition comprising PolarTherm® 160 boron nitride powder and/or ORPAC BORON NITRIDE RELEASECOAT-CONC dispersion, RD-847A polyester, PVP K-30 polyvinyl pyrrolidone, DESMOPHEN 2000 polyester, A-174 acrylic-functional organo silane coupling agent, A-187 epoxy-functional organo silane coupling agent, PLURONICS F-108 polyoxypropylene-polyoxyethylene copolymer, VERSAMID 140 polyamide, and MACOL NP-6 nonyl phenol.

In still another embodiment for weaving fabric for laminated printed circuit boards, glass fibers of the coated fiber strand of the present invention have a primary layer of a dried residue of an aqueous primary sizing composition comprising ROPAQUE® HP-1055 and/or ROPAQUE® OC-96 styrene-acrylic copolymer hollow spheres, PVP K-30 polyvinyl pyrrolidone, A-174 acrylic-functional organo silane coupling agents and A-187 epoxy-functional organo silane coupling agents, EMERY® 6717 partially amidated polyethylene imine, STEPANTEX 653 cetyl palmitate, TMAZ 81 ethylene oxide derivatives of sorbitol esters, MACOL OP-10 ethoxylated alkylphenol and MAZU DF-136 antifoaming material. In addition, this embodiment can optionally further include PolarTherm® 160 boron nitride powder and/or ORPAC BORON NITRIDE RELEASECOAT-CONC dispersion.

The coating compositions useful in the present invention can be prepared by any suitable method such as conventional mixing well known to those skilled in the art. Preferably, the components discussed above are diluted with water to have the desired weight percent solids and mixed together. Powdered particles can be premixed with water or added to the polymeric material prior to mixing with the other components of the coating.

The layer of coating is applied to the fibers in many ways, for example by contacting the filaments with a roller or belt applicator, spraying or other means. The coated fibers are preferably dried at room temperature or at elevated temperatures. The dryer removes excess moisture from the fibers and, if present, cures any curable coating composition components. The temperature and time for drying the glass fibers will depend upon such variables as the percentage of solids in the coating composition, components of the coating composition and type of glass fiber. The coating composition is typically present as a dried sizing residue on the fibers in an amount between about 0.1 percent and about 25 percent by weight after drying. The loss on ignition of the fibers is generally less than about 1.0 weight percent, preferably less than about 0.5 weight percent, and more preferably ranges from about 0.01 to about 0.45 weight percent. As used herein the term "loss on ignition" means the weight percent of dried coating composition present on the surface of the fiber strand as determined by the following equation:

$$LOI = 100 \times [(W_{dry} - W_{bare})/W_{dry}]$$

wherein W_{dry} is the weight of the fiber strand plus the residue of the coating composition after drying in an oven at about 220°F (about 104°C) for about 60 minutes and W_{bare} is the weight of the bare fiber strand after removal of residue of the coating composition by heating the fiber strand in an oven at about 1150°F (about 621°C) for about 20 minutes.

A layer of a secondary coating composition can be applied over the layer of coating composition discussed above in an amount effective to coat or impregnate the portion of the coated strands, for example by dipping the coated strand in a bath containing the secondary coating composition, spraying the secondary coating composition upon the coated strand or by contacting the coated strand with an applicator as discussed above. The coated strand can be passed through a die to remove excess coating composition from the strand and/or dried as discussed above for a time

sufficient to at least partially dry or cure the secondary coating composition. The method and apparatus for applying the secondary coating composition to the strand is determined in part by the configuration of the strand material. The strand is preferably dried after application of the secondary coating composition in a manner well known in the art.

Suitable secondary coating compositions can include one or more film-forming materials, lubricants and other additives such as are discussed above. The secondary coating is preferably different from the sizing composition, i.e., it (1) contains at least one component which is chemically different from the components of the sizing composition; or (2) contains at least one component in an amount which is different from the amount of the same component contained in the sizing composition. Non-limiting examples of suitable secondary coating compositions including polyurethane are disclosed in U.S. Patent Nos. 4,762,750 and 4,762,751, which are hereby incorporated by reference.

In an alternative embodiment of the present invention, the glass fibers of the fiber strand can having applied thereto a primary coating of a dried residue of a conventional sizing composition or a sizing composition which can include any of the sizing components in the amounts discussed above. Examples of suitable sizing compositions are set forth in Loewenstein at pages 237-291 (3d Ed. 1993) and U.S. Patent Nos. 4,390,647 and 4,795,678, each of which is hereby incorporated by reference. A layer of a secondary coating composition useful in the present invention and disclosed herein is applied to at least a portion, and preferably over the entire outer surface, of the primary coating. The secondary coating composition can comprise one or more types of particles discussed above and/or those that are set forth in Tables B below. It is noted that several of these particles have a Mohs hardness greater than that expected for the glass fiber, i.e. about 4.5 to about 6. However, since these particles are part of the secondary coating composition that does not directly contact the surface of the glass fibers,

these higher hardnesses will not adversely affect the glass fibers and are acceptable.

Table B

Inorganic Solid Material	Thermal conductivity (W/m K at 300K)	Electrical Resistance (micro ohm-centimeters)	Mohs' hardness (original scale)
boron nitride	about 200[29]	1.7×10^{19}[30]	about 2[31]
boron phosphide	about 350[32]	-	about 9.5[33]
Aluminum phosphide	about 130[34]	-	-
aluminum nitride	about 200[35]	greater than 10^{19}[36]	about 9[37]
gallium nitride	about 170[38]	-	-
gallium phosphide	about 100[39]	-	-
silicon carbide	about 270[40]	4×10^{5} to 1×10^{6}[41]	greater than 9[42]
silicon nitride	about 30[43]	10^{19} to 10^{20}[44]	about 9[45]
beryllium oxide	about 240[46]	-	about 9[47]
zinc oxide	about 26	-	about 4.5[48]
zinc sulfide	about 25[49]	2.7×10^{5} to 1.2×10^{12}[50]	about 3.5-4[51]

29 G. Slack, "Nonmetallic Crystals with High Thermal Conductivity, J. Phys. Chem. Solids (1973) Vol. 34, p. 322, which is hereby incorporated by reference.
30 A. Weimer (Ed.), Carbide, Nitride and Boride Materials Synthesis and Processing, (1997) at page 654.
31 Friction, Wear, Lubrication at page 27.
32 G. Slack, "Nonmetallic Crystals with High Thermal Conductivity, J. Phys. Chem. Solids (1973) Vol. 34, p. 325, which is hereby incorporated by reference.
33 R. Lewis, Sr., Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 164, which is hereby incorporated by reference.
34 G. Slack, "Nonmetallic Crystals with High Thermal Conductivity, J. Phys. Chem. Solids (1973) Vol. 34, p. 333, which is hereby incorporated by reference
35 G. Slack, "Nonmetallic Crystals with High Thermal Conductivity, J. Phys. Chem. Solids (1973) Vol. 34, p. 329, which is hereby incorporated by reference.
36 A. Weimer (Ed.), Carbide, Nitride and Boride Materials Synthesis and Processing, (1997) at page 654.
37 Friction, Wear, Lubrication at page 27.
38 G. Slack, "Nonmetallic Crystals with High Thermal Conductivity, J. Phys. Chem. Solids (1973) Vol. 34, p. 333
39 G. Slack, "Nonmetallic Crystals with High Thermal Conductivity, J. Phys. Chem. Solids (1973) Vol. 34, p. 321, which is hereby incorporated by reference.
40 Microelectronics Packaging Handbook at page 36, which is hereby incorporated by reference.
41 A. Weimer (Ed.), Carbide, Nitride and Boride Materials Synthesis and Processing, (1997) at page 653, which is hereby incorporated by reference.
42 Friction, Wear, Lubrication at page 27.
43 Microelectronics Packaging Handbook at page 36, which is hereby incorporated by reference.
44 A. Weimer (Ed.), Carbide, Nitride and Boride Materials Synthesis and Processing, (1997) at page 654.
45 Friction, Wear, Lubrication at page 27.
46 Microelectronics Packaging Handbook at page 905, which is hereby incorporated by reference.
47 Hawley's Condensed Chemical Dictionary, (12th Ed. 1993) at page 141, which is hereby incorporated by reference.
48 Friction, Wear, Lubrication at page 27.
49 Handbook of Chemistry and Physics, CRC Press (1975) at page 12-54.
50 Handbook of Chemistry and Physics, CRC Press (71st Ed. 1990) at page 12-63, which is hereby incorporated by reference.

Table B (cont'd)

Inorganic Solid Material	Thermal conductivity (W/m K at 300K)	Electrical Resistance (micro ohm-centimeters)	Mohs' hardness (original scale)
diamond	about 2300[52]	2.7×10^{8} [53]	10[54]
silicon	about 84[55]	about 10.0[56]	about 7[57]
graphite	up to 2000[58]	100[59]	about 0.5-1[60]
molybdenum	about 138[61]	about 5.2[62]	about 5.5[63]
platinum	about 69[64]	about 10.6[65]	about 4.3[66]
palladium	about 70[67]	about 10.8[68]	about 4.8[69]
tungsten	about 200[70]	about 5.5[71]	about 7.5[72]
nickel	about 92[73]	about 6.8[74]	about 5[75]
aluminum	about 205[76]	about 4.3[77]	about 2.5[78]
chromium	about 66[79]	about 20[80]	about 9.0[81]
copper	about 398[82]	about 1.7[83]	about 2.5-3[84]

51 Handbook of Chemistry and Physics, CRC Press (71st Ed. 1990) at page 4-158, which is hereby incorporated by reference.
52 Microelectronics Packaging Handbook at page 36.
53 Handbook of Chemistry and Physics, CRC Press (71st Ed. 1990) at page 12-63, which is hereby incorporated by reference.
54 Handbook of Chemistry and Physics at page F-22.
55 Microelectronics Packaging Handbook at page 174.
56 Handbook of Chemistry and Physics at page F-166, which is hereby incorporated by reference.
57 Friction, Wear, Lubrication at page 27.
58 G. Slack, "Nonmetallic Crystals with High Thermal Conductivity, J. Phys. Chem. Solids (1973) Vol. 34, p. 322, which is hereby incorporated by reference.
59 See W. Callister, Materials Science and Engineering An Introduction, (2d ed. 1991) at page 637, which is hereby incorporated by reference.
60 Handbook of Chemistry and Physics at page F-22.
61 Microelectronics Packaging Handbook at page 174.
62 Microelectronics Packaging Handbook at page 37.
63 According to "Web Elements" http://www.shef.ac.uk/~chem/web-elents/nofr-image-l/hardness-minerals-l.html (February 26, 1998).
64 Microelectronics Packaging Handbook at page 174.
65 Microelectronics Packaging Handbook at page 37.
66 Handbook of Chemistry and Physics at page F-22.
67 Microelectronics Packaging Handbook at page 37.
68 Microelectronics Packaging Handbook at page 37.
69 Handbook of Chemistry and Physics at page F-22.
70 Microelectronics Packaging Handbook at page 37.
71 Microelectronics Packaging Handbook at page 37.
72 According to "Web Elements" http://www.shef.ac.uk/~chem/web-elents/nofr-image-l/hardness-minerals-l.html (February 26, 1998).
73 Microelectronics Packaging Handbook at page 174.
74 Microelectronics Packaging Handbook at page 37.
75 Handbook of Chemistry and Physics at page F-22.
76 Microelectronics Packaging Handbook at page 174.
77 Microelectronics Packaging Handbook at page 37.
78 Friction, Wear, Lubrication at page 27.
79 Microelectronics Packaging Handbook at page 37.
80 Microelectronics Packaging Handbook at page 37.
81 Handbook of Chemistry and Physics at page F-22.
82 Microelectronics Packaging Handbook at page 174.
83 Microelectronics Packaging Handbook at page 37.
84 Handbook of Chemistry and Physics, at page F-22.

Table B (cont'd)

Inorganic Solid Material	Thermal conductivity (W/m K at 300K)	Electrical Resistance (micro ohm-centimeters)	Mohs' hardness (original scale)
gold	about 297[85]	about 2.2[86]	about 2.5-3[87]
iron	about 74.5[88]	about 9[89]	about 4-5[90]
silver	about 418[91]	about 1.6[92]	about 2.5-4[93]

Molybdenum disulfide and magnesium oxide are other inorganic particles that are useful for secondary or tertiary coatings useful in the present invention. One skilled in the art would understand that mixtures of any of the above inorganic particles can be used in the present invention.

In an alternative embodiment, the particles of the secondary coating composition comprise hydrophilic inorganic particles that absorb and retain water in the interstices of the hydrophilic particles. The hydrophilic inorganic particles can absorb water or swell when in contact with water or participate in a chemical reaction with the water to form, for example, a viscous gel-like solution which blocks or inhibits further ingress of water into the interstices of a telecommunications cable which the coated glass fiber strand is used to reinforce. As used herein, "absorb" means that the water penetrates the inner structure or interstices of the hydrophilic material and is substantially retained therein. See Hawley's Condensed Chemical Dictionary at page 3, which is hereby incorporated by reference. "Swell" means that the hydrophilic particles expand in size or volume. See Webster's New Collegiate Dictionary (1977) at page 1178, which is hereby incorporated by reference. Preferably, the hydrophilic particles swell after contact with water to at least one and one-half times their original dry weight, and more preferably about two to about six

---

85 Microelectronics Packaging Handbook at page 174.
86 Microelectronics Packaging Handbook at page 37.
87 Handbook of Chemistry and Physics at page F-22.
88 Microelectronics Packaging Handbook at page 174.
89 Handbook of Chemistry and Physics, CRC Press (1975) at page D-171, which is hereby incorporated by reference.
90 Handbook of Chemistry and Physics at page F-22.
91 Microelectronics Packaging Handbook at page 174.
92 Microelectronics Packaging Handbook at page 37.
93 Handbook of Chemistry and Physics at page F-22.

times their original weight. Non-limiting examples of hydrophilic inorganic solid lubricant particles that swell include smectites such as vermiculite and montmorillonite, absorbent zeolites and inorganic absorbent gels. Preferably, these hydrophilic particles are applied in powder form over tacky sizing or other tacky secondary coating materials. The amount of hydrophilic inorganic particles in this embodiment of the secondary coating composition can range from about 1 to about 99 weight percent on a total solids basis and preferably about 20 to about 90 weight percent.

The amount of inorganic particles in the secondary coating composition can range from about 1 to about 99 weight percent on a total solids basis, and preferably about 20 to about 90 weight percent. The percentage of solids of an aqueous secondary coating composition generally ranges from about 5 to about 75 weight percent.

In another alternative embodiment of the present invention, a layer of a tertiary coating composition is applied over at least a portion of the surface, and preferably over the entire surface, of a secondary coating, i.e., such a fiber strand would have a layer of a primary coating of sizing, a layer of a secondary coating composition and an outer layer of the tertiary coating. The tertiary coating is preferably different from the sizing composition and the secondary coating composition, i.e., the tertiary coating composition (1) contains at least one component which is chemically different from the components of the sizing and secondary coating composition; or (2) contains at least one component in an amount which is different from the amount of the same component contained in the sizing or secondary coating composition. The tertiary coating is applied to the glass fibers and strands prior to or after incorporation into a fabric using techniques, such as but not limiting to, spraying and dipping as discussed earlier and as are well know in the art.

In this embodiment, the secondary coating composition comprises one or more polymeric materials discussed above, such as polyurethane, and the

tertiary coating composition comprises powdered thermally conductive inorganic particles, such as the PolarTherm® boron nitride particles, or hollow particles, such as ROPAQUE® pigment, which are discussed above. Preferably, the powdered coating is applied by passing the strand having a liquid secondary coating composition applied thereto through a fluidized bed or spray device to adhere the powder particles to the tacky secondary coating composition. Alternatively, the strands can be assembled into a fabric 114 before the layer 140 of tertiary coating is applied, as shown in Fig. 4. The weight percent of powdered, thermally conductive inorganic particles adhered to the coated strand can range from about 0.1 to about 75 weight percent of the total weight of the dried strand. The tertiary coating can also include one or more polymeric materials such as are discussed above, such as acrylic polymers, epoxies, or polyolefins, conventional stabilizers and other modifiers known in the art of such coatings, preferably in dry powdered form.

Although the prior discussion is generally directed toward applying the coating composition of the present invention directly on glass fibers after fiber forming and subsequently incorporating the fibers into a fabric, it should be appreciated by those skilled in the art that the present invention also includes an embodiment wherein the coating composition of the present invention is applied to a fabric after it has been manufactured using various techniques well known in the art. Depending on the processing of the fabric, the coating composition of the present invention can be applied either directly to the glass fibers in the fabric or to another coating already on the glass fibers and/or fabric. For example, the glass fibers can be coated with a conventional starch-oil sizing after forming and woven into a fabric. The fabric can then be treated to remove the starch-oil sizing. A coating composition useful in the present invention and disclosed herein can thereafter be applied directly to the fabric using well known techniques, such as but not limited to, spraying or dipping the fabric into a bath of the sizing composition. The fabric can then be dried prior to further processing to leave a residue of the composition on

the fibers and strands of the fabric.. This sizing removal is accomplished using techniques well known in the art, such as thermal treatment or washing of the fabric. In this instance, the coating composition would directly coat the surface of the fibers of the fabric. If any portion of the sizing composition initially applied to the glass fibers after forming is not removed, the coating composition of the present invention would then be applied over the remaining portion of the sizing composition rather than directly to the fiber surface.

In another embodiment of the present invention, selected components of the coating composition of the present invention are applied to the glass fibers immediately after forming and the remaining components of the coating composition are applied to the fabric after it is made. In a manner similar to that discussed above, some or all of the selected components can be removed from the glass fibers prior to coating the fibers and fabric with the remaining components. As a result, the remaining components will either directly coat the surface of the fibers of the fabric or coat those selected components that were not removed from the fiber surface.

The woven fabric 14 is used as a reinforcement for reinforcing polymeric matrix materials 12 to form a composite or laminate 10, such as is shown in Fig. 1, preferably for use in electronic circuit boards. The warp and weft (i.e. fill) strands of fabric 14 can be non-twisted (also referred to as untwisted or zero twist) or twisted prior to weaving by any conventional twisting technique known to those skilled in the art, for example by using twist frames to impart twist to the strand at about 0.5 to about 3 turns per inch. In addition, the fabric 14 can include various combinations of both twisted and non-twisted warp and weft strands.

The reinforcing fabric 14 can include about 5 to about 100 warp strands per centimeter (about 13 to about 254 warp strands per inch) and preferably has about 6 to about 50 weft strands per centimeter (about 15 to

about 127 weft strands per inch). The weave construction can be a regular plain weave, although any other weaving style well known to those skilled in the art, such as a twill weave or satin weave, can be used.

The fabric 14 is preferably woven in a style which is suitable for use in a laminate for printed circuit boards, such as are disclosed in "Fabrics Around the World", a technical bulletin of Clark-Schwebel, Inc. of Anderson, South Carolina (1995), which is hereby incorporated by reference. A non-limiting example of a fabric style using E225 E-glass fibers is Style 2116, which has 118 warp yarns and 114 weft yarns per 5 centimeters (60 warp yarns and 58 weft yarns per inch); uses 7 22 1x0 (E225 1/0) warp and weft yarn; has a nominal fabric thickness of 0.094 mm (0.037 inches); and a fabric weight of 103.8 g/m^2 (3.06 ounces per square yard). A non-limiting example of a fabric style using G75 E-glass fibers is Style 7628, which has 87 warp yarns and 61 weft yarns per 5 centimeters (44 warp yarns and 31 weft yarns per inch); uses 9 68 1x0 (G75 1/0) warp and weft yarn; has a nominal fabric thickness of 0.173 mm (0.0068 inches); and a fabric weight of 203.4 g/m^2 (6.00 ounces per square yard). A non-limiting example of a fabric style using D450 E-glass fibers is Style 1080, which has 118 warp yarns and 93 weft yarns per 5 centimeters (60 warp yarns and 47 weft yarns per inch); uses 5 11 1x0 (D450 1/0) warp and weft yarn; has a nominal fabric thickness of 0.053 mm (0.0021 inches); and a fabric weight of 46.8 g/m^2 (1.38 ounces per square yard). A non-limiting example of a fabric style using D900 E-glass fibers is Style 106, which has 110 warp yarns and 110 weft yarns per 5 centimeters (56 warp yarns and 56 weft yarns per inch); uses 5 5.5 1x0 (D900 1/0) warp and weft yarn; has a nominal fabric thickness of 0.033 mm (0.013 inches); and a fabric weight of 24.4 g/m^2 (0.72 ounces per square yard). Another non-limiting example of a fabric style using D900 E-glass fibers is Style 108, which has 118 warp yarns and 93 weft yarns per 5 centimeters (60 warp yarns and 47 weft yarns per inch); uses 5 5.5 1x2 (D900 1/2) warp and weft yarn; has a nominal fabric thickness of 0.061 mm (0.0024 inches); and a

fabric weight of 47.5 g/m^2 (1.40 ounces per square yard). A non-limiting example of a fabric style using both E225 and D450 E-glass fibers is Style 2113, which has 118 warp yarns and 110 weft yarns per 5 centimeters (60 warp yarns and 56 weft yarns per inch); uses 7 22 1x0 (E225 1/0) warp yarn and 5 11 1x0 (D450 1/0) weft yarn; has a nominal fabric thickness of 0.079 mm (0.0031 inches); and a fabric weight of 78.0 g/m^2 (2.30 ounces per square yard). A non-limiting example of a fabric style using both G50 and G75 E-glass fiber yarns is Style 7535 which has 87 warp yarns and 57 fill yarns per 5 centimeters (44 warp yarns and 29 fill yarns per inch); uses 9 68 1x0 (G75 1/0) warp yarn and 9 99 1x0 (G50 1/0) fill yarn; has a nominal fabric thickness of about 0.201 millimeters (about 0.0079 inches); and a fabric weight of about 232.3 grams per square meter (about 6.85 ounces per square yard). These and other useful fabric style specifications are given in IPC-EG-140 "Specification for Finished Fabric Woven from 'E' Glass for Printed Boards", a publication of The Institute for Interconnecting and Packaging Electronic Circuits (June 1997), which is hereby incorporated by reference. Although the aforementioned fabric styles use twisted yarns, it is contemplated that these or other fabric styles using zero-twist yarns or rovings in conjunction with or in lieu of twisted yarns can be made in accordance with the present invention. It is further contemplated that some or all of the warp yarn in the fabric can have fibers coated with a first resin compatible sizing composition and some or all of the fill yarn can have fibers coated with a second resin compatible coating different from the first composition, i.e. the second composition (1) contains at least one component which is chemically different from the components of the first sizing composition; or (2) contains at least one component in an amount which is different from the amount of the same component contained in the first sizing composition.

A suitable woven reinforcing fabric 14 useful in the present invention is formed by using any conventional loom well known to those skilled in the art,

such as a shuttle loom or rapier loom, but preferably is formed using an air jet loom. In weaving a fabric using the air jet process, the air jet loom inserts the fill yarn into the warp shed and propels the yarn across the width of the fabric by a blast of compressed air from one or more air jet. Preferred air jet looms are commercially available from Tsudakoma of Japan as Model No. 103, 103I and 1033 and Sulzer Ruti Model No. L-5000, L-5100 L-5200 which are commercially available from Sulzer Brothers Ltd. of Zurich, Switzerland. Sulzer Ruti L-5000, L-5100 and L-5200 Product Bulletins of Sulzer Ruti Ltd., Switzerland, which are hereby incorporated by reference.

Referring now to Fig. 1, the fabric 14 is used to form a laminate 10 by coating and/or impregnating one or more layers of the fabric 14 with a polymeric thermoplastic or thermosetting matrix material 12. The laminate 10 is suitable for use as an electronic support.

Matrix materials useful in the present invention include thermosetting materials such as thermosetting polyesters, vinyl esters, epoxides (containing at least one epoxy or oxirane group in the molecule, such as polyglycidyl ethers of polyhydric alcohols or thiols), phenolics, aminoplasts, thermosetting polyurethanes, derivatives and mixtures thereof. Preferred matrix materials for forming laminates for electronic circuit boards are FR-4 epoxy resins, polyimides and liquid crystalline polymers, the compositions of that are well know to those skilled in the art. If further information regarding such compositions is needed, see 1 Electronic Materials Handbook™, ASM International (1989) at pages 534-537.

Non-limiting examples of suitable thermoplastic polymeric matrix materials include polyolefins, polyamides, thermoplastic polyurethanes and thermoplastic polyesters, vinyl polymers and mixtures thereof. Further examples of useful thermoplastic materials include polyimides, polyether sulfones, polyphenyl sulfones, polyetherketones, polyphenylene oxides, polyphenylene sulfides, polyacetals, polyvinyl chlorides and polycarbonates.

A useful matrix material formulation consists of EPON 1120-A80 epoxy resin, dicyandiamide, 2-methylimidazole and DOWANOL PM.

Other components which can be included with the polymeric matrix material and reinforcing material in the composite include colorants or pigments, lubricants or processing aids, ultraviolet light (UV) stabilizers, antioxidants, other fillers and extenders.

The fabric 14 can be coated and impregnated by dipping the fabric 14 in a bath of the polymeric matrix material 12, for example, as discussed in R. Tummala (Ed.), Microelectronics Packaging Handbook, (1989) at pages 895-896, which are hereby incorporated by reference. The polymeric matrix material 12 and fabric 14 can be formed into a composite or laminate 10 by a variety of methods which are dependent upon such factors as the type of polymeric matrix material used. For example, for a thermosetting matrix material, the laminate can be formed by compression or injection molding, pultrusion, hand lay-up, or by sheet molding followed by compression or injection molding. Thermosetting polymeric matrix materials is cured by the inclusion of crosslinkers in the matrix material and/or by the application of heat, for example. Suitable crosslinkers useful to crosslink the polymeric matrix material are discussed above. The temperature and curing time for the thermosetting polymeric matrix material depends upon such factors as the type of polymeric matrix material used, other additives in the matrix system and thickness of the composite, to name a few.

For a thermoplastic matrix material, suitable methods for forming the composite include direct molding or extrusion compounding followed by injection molding. Methods and apparatus for forming the composite by the above methods are discussed in I. Rubin, Handbook of Plastic Materials and Technology (1990) at pages 955-1062, 1179-1215 and 1225-1271, which are hereby incorporated by reference.

Although not limiting in the present invention, in one embodiment shown in Fig. 5, composite or laminate 210 includes fabric 214 impregnated

with a compatible matrix material 212. The impregnated fabric can then be squeezed between a set of metering rolls or bars to leave a measured amount of matrix material, and dried to form an electronic support in the form of a semicured substrate or prepreg. An electrically conductive layer 250 is positioned along a portion of a side 252 of the prepreg in a manner to be discussed below in the specification, and the prepreg is cured to form a laminate 210 which functions as an electronic support 254 with an electrically conductive layer. In another embodiment of the invention, and more typically in the electronic support industry, two or more prepregs are combined with one or more electrically conductive layers and laminated together and cured in a manner well known to those skilled in the art, to form an electronic support. For example, but not limiting the present invention, the prepreg stack is laminated by pressing the stack, e.g. between polished steel plates, at elevated temperatures and pressures for a predetermined length of time to cure the polymeric matrix and form a laminate of a desired thickness. A portion of one or more of the prepregs can be provided with an electrically conductive layer either prior to or after lamination and curing such that the resulting electronic support is a laminate having at least one electrically conductive layer along a portion of an exposed surface (hereinafter referred to as a "clad laminate").

Circuits can then be formed from the electrically conductive layer(s) of the single layer or multilayered electronic support using techniques well known in the art to construct an electronic support in the form of an electronic circuit board.

If desired, apertures or holes (also referred to as "vias") are formed in the electronic supports, to allow for electrical interconnection between circuits and/or components on opposing surfaces of the electronic support, by any convenient manner known in the art, including but not limited to mechanical drilling and laser drilling. More specifically, referring to Fig. 6, an aperture 360 extends through at least one layer 362 of fabric 312 of an electronic support

354 of the present invention. The fabric 312 comprises coated fiber strands comprising at least one glass fiber having a layer that is compatible with a variety of polymeric matrix materials as taught herein. In forming the aperture 360, electronic support 354 is positioned in registry with an aperture forming apparatus, such as a drill bit 364 or laser tip. The aperture 360 is formed through a portion 366 of the at least one layer 362 of fabric 312 by drilling using the drill 364 or laser. After formation of the apertures, a layer of electrically conductive material is deposited on the walls of the aperture or the aperture is filled with an electrically conductive material to facilitate the required electrical interconnection between one or more electrically conductive layers (not shown in Fig. 6) on the surface of the electronic support 354 and/or heat dissipation.

The electrically conductive layer, for example as shown in Figure 5 as layer 250, can be formed by any method well known to those skilled in the art. For example but not limiting the present invention, the electrically conductive layer is formed by laminating a thin sheet or foil of metallic material onto at least a portion of a side of the semi-cured or cured prepreg or laminate. As an alternative, the electrically conductive layer is formed by depositing a layer of metallic material onto at least a portion of a side of the semi-cured or cured prepreg or laminate using well known techniques including but not limited to electrolytic plating, electroless plating or sputtering. Metallic materials suitable for use as an electrically conductive layer include but are not limited to copper (which is preferred), silver, aluminum, gold, tin, tin-lead alloys, palladium and combinations thereof.

In another embodiment of the present invention, the electronic support is in the form of a multilayered electronic circuit board constructed by laminating together one or more electronic circuit boards (described above) with one or more clad laminates (described above) and/or one or more prepregs (described above). If desired, additional electrically conductive layers can be incorporated into the electronic support, for example along a

portion of an exposed side of the multilayered electronic circuit board. Furthermore, if required, additional circuits can be formed from the electrically conductive layers in a manner discussed above. It should be appreciated that depending on the relative positions of the layers of the multilayered electronic circuit board, the board can have both internal and external circuits. Additional apertures can be formed, as discussed earlier, partially through or completely through the board to allow electrical interconnection between the layers at selected locations. It should be appreciated that the resulting structure can have some apertures that extend completely through the structure, some apertures that extend only partially through the structure, and some apertures that are completely within the structure.

Preferably, the thickness of the laminate forming the electronic support 254 is greater than about 0.051 mm (0.002 inches), and more preferably ranges from about 0.13 mm (0.005 inches) to about 2.5 mm (about 0.1 inches). For an eight ply laminate of 7628 style fabric, the thickness is generally about 1.32 mm (0.052 inches). The number of layers of fabric 14 in the laminate 10 can vary based upon the desired thickness of the laminate.

The resin content of the laminate can range from about 35 to about 80 weight percent, and more preferably about 40 to about 75 weight percent. The amount of fabric in the laminate can range from about 20 to about 65 weight percent and more preferably ranges from about 25 to about 60 weight percent.

For a laminate formed from woven E-glass fabric and using an FR-4 epoxy resin matrix material having a minimum glass transition temperature of about 110°C, the desired minimum flexural strength in the cross machine or width direction (generally perpendicular to the longitudinal axis of the fabric) is greater than 3×10^7 kg/m^2, preferably greater than about 3.52×10^7 kg/m^2 (about 50 Kpsi), and more preferably greater than about 4.9×10^7 kg/m^2 (about 70 Kpsi) according to IPC-4101 "Specification for Base Materials for Rigid and Multilayer Printed Boards" at page 29, a publication of The Institute

for Interconnecting and Packaging Electronic Circuits (December 1997). IPC-4101 is hereby incorporated by reference in its entirety. In the length direction, the desired minimum flexural strength in the length direction (generally parallel to the longitudinal axis of the fabric) is greater than about 4 x 10^7 kg/m^2, and preferably greater than 4.23 x 10^7 kg/m^2. The flexural strength is measured according to ASTM D-790 and IPC-TM-650 Test Methods Manual of the Institute for Interconnecting and Packaging Electronics (December 1994) (which are hereby incorporated by reference) with metal cladding completely removed by etching according to section 3.8.2.4 of IPC-4101. Advantages of the electronic supports of the present invention include high flexural strength (tensile and compressive strength) and high modulus, which can lessen deformation of a circuit board including the laminate.

Electronic supports of the present invention in the form of copper clad FR-4 epoxy laminates preferably have a coefficient of thermal expansion from 50°C to 288°C in the z-direction of the laminate ("Z-CTE"), i.e., across the thickness of the laminate, of less than about 5.5 percent, and more preferably ranging from about 0.01 to about 5.0 weight percent, according to IPC Test Method 2.4.41 (which is hereby incorporated by reference). Each such laminate preferably contains eight layers of 7628 style fabric, although styles 106, 108, 1080, 2113, 2116 or 7535 style fabrics can alternatively be used. In addition, the laminate can incorporate combinations of these fabric styles. Laminates having low coefficients of thermal expansion are generally less susceptible to expansion and contraction and can minimize board distortion.

The instant invention further contemplates the fabrication of multilayered laminates and electronic circuit boards which include at least one composite layer made according to the teachings herein and at least one composite layer made in a manner different from the composite layer taught herein, e.g. made using conventional glass fiber composite technology. More specifically and as is well known to those skilled in the art, traditionally the

filaments in continuous glass fiber strands used in weaving fabric are treated with a starch/oil sizing which includes partially or fully dextrinized starch or amylose, hydrogenated vegetable oil, a cationic wetting agent, emulsifying agent and water, including but not limited to those disclosed in Loewenstein at pages 237-244 (3d Ed. 1993), which is hereby incorporated by reference. Warp yarns produced from these strands are thereafter treated with a solution prior to weaving to protect the strands against abrasion during the weaving process, e.g. poly(vinyl alcohol) as disclosed in U.S. Patent No. 4,530,876 at column 3, line 67 through column 4, line 11, which is hereby incorporated by reference. This operation is commonly referred to as slashing. The poly(vinyl alcohol) as well as the starch/oil size are generally not compatible with the polymeric matrix material used by composite manufacturers and the fabric must be cleaned to remove essentially all organic material from the surface of the glass fibers prior to impregnating the woven fabric. This can be accomplished in a variety ways, for example by scrubbing the fabric or, more commonly, by heat treating the fabric in a manner well known in the art. As a result of the cleaning operation, there is no suitable interface between the polymeric matrix material used to impregnate the fabric and the cleaned glass fiber surface, so that a coupling agent must be applied to the glass fiber surface. This operation is sometime referred to by those skilled in the art as finishing. The coupling agents most commonly used in finishing operations are silanes, including but not limited to those disclosed in E. P. Plueddemann, Silane Coupling Agents (1982) at pages 146-147, which is hereby incorporated by reference. Also see Loewenstein at pages 249-256 (3d Ed. 1993). After treatment with the silane, the fabric is impregnated with a compatible polymeric matrix material, squeezed between a set of metering rolls and dried to form a semicured prepreg as discussed above. It should be appreciated that depending on the nature of the sizing, the cleaning operation and/or the matrix resin used in the composite, the slashing and/or finishing steps can be eliminated. One or more prepregs incorporating conventional

glass fiber composite technology can then be combined with one or more prepregs incorporating the instant invention to form an electronic support as discussed above, and in particular a multilayered laminate or electronic circuit board. For more information regarding fabrication of electronic circuit boards, see 1 Electronic Materials Handbook™, ASM International (1989) at pages 113-115, R. Tummala (Ed.), Microelectronics Packaging Handbook, (1989) at pages 858-861 and 895-909, M. W. Jawitz, Printed Circuit Board Handbook (1997) at pages 9.1-9.42, and C. F. Coombs, Jr. (Ed.), Printed Circuits Handbook, (3d Ed. 1988), pages 6.1-6.7, which are hereby incorporated by reference.

The composites and laminates forming the electronic supports of the instant invention can be used to form packaging used in the electronics industry, and more particularly first, second and/or third level packaging, such as that disclosed in Tummala at pages 25-43, which is hereby incorporated by reference. In addition, the present invention can also be used for other packaging levels.

The present invention will now be illustrated by the following specific, non-limiting examples.

EXAMPLE 1

Electrical grade laminates made from prepregs incorporating fabrics with yarns having different sizing compositions were tested to evaluate their drilling properties, and more specifically, (i) the drill tip wear of drills used to drill holes through the laminates and (ii) the locational accuracy of the holes drilled through the laminates. Control A and Sample B were laminates incorporating a 7628 style fabric as discussed earlier. The fabric in Control A was a heat cleaned and silane finished fabric commercially available from Clark Schwebel and identified as 7628-718. The fabric in Sample B was woven from yarn comprising glass fibers coated with a resin compatible sizing

as taught herein and shown in Table 1. The glass fibers woven into Sample B had a loss on ignition of 0.35 percent.

Table 1
Weight Percent of Components on Total Solids Basis for Sizing used in Sample B

COMPONENT	Sample B
thermoplastic polyester film-forming polymer[94]	27.0
thermoplastic polyester film-forming polymer [95]	36.2
polyvinyl pyrrolidone[96]	9.0
epoxy-functional organo silane coupling agent[97]	2.1
acrylic-functional organo silane coupling agent[98]	4.4
polyoxyalkylene block copolymer[99]	9.0
polyamide[100]	4.4
emulsifying agent[101]	5.4
boron nitride powder particles[102]	0.9
25 wt% boron nitride aqueous dispersion[103]	1.5
acetic acid	<0.1

[94] RD-847A polyester resin, which is commercially available from Borden Chemicals of Columbus, Ohio.
[95] DESMOPHEN 2000 polyethylene adipate diol, which is commercially available from Bayer of Pittsburgh, Pennsylvania.
[96] PVP K-30 polyvinyl pyrrolidone, which is commercially available from ISP Chemicals of Wayne, New Jersey.
[97] A-187 gamma-glycidoxypropyltrimethoxysilane, which is commercially available from OSi Specialties, Inc. of Tarrytown, New York.
[98] A-174 gamma-methacryloxypropyltrimethoxysilane, which is commercially available from OSi Specialties, Inc. of Tarrytown, New York.
[99] PLURONIC™ F-108 polyoxypropylene-polyoxyethylene copolymer, which is commercially available from BASF Corporation of Parsippany, New Jersey.
[100] VERSAMID 140 polyamide, which is commercially available from General Mills Chemicals, Inc.
[101] MACOL NP-6 nonyl phenol surfactant, which is commercially available from BASF of Parsippany, New Jersey.
[102] PolarTherm® PT 160 boron nitride powder particles, which are commercially available from Advanced Ceramics Corporation of Lakewood, Ohio.
[103] ORPAC BORON NITRIDE RELEASECOAT-CONC, which is commercially available from ZYP Coatings, Inc. of Oak Ridge,

Prepregs were prepared by a hand lay-up procedure that involved applying standard FR-4 epoxy resin (EPON 1120-A80 resin available from Shell Chemical co.) to the fabrics using a paintbrush. The resin saturated fabric was immediately "dried" and B-stages in a vented hot air oven for about 3 to about 3.25 minutes at 163°C (325°F) until the desired gel time of 124 seconds at 171°C (340°F) was reached. The prepregs were trimmed to 46 cm by 46 cm (18 inch by 18 inch) sections and weighed to determine resin content. Only prepregs with resin contents of 44 percent ± 2 percent were used in the subsequent laminating procedure.

Prepregs were stacked 8 high and molded in a Wabash Press for 70 minutes at 177°C (350°F) and at 345 newtons/cm^2 (500 psi). All the laminates were molded without copper foil layers. The laminates showed various levels of air entrapment. It is believed that the lack of vacuum assist and temperature ramping during lamination contributed to this condition.

Tool Wear Analysis

The first series of tests were conducted to evaluate the wear of the drill tip. The tip wear was expressed in terms of "drill tip percent wear" which was calculated using the formula:

drill tip percent wear = $100 \times (P_i - P_f)/P_i$

where P_i = initial width of the primary cutting edge

P_f = width of the primary cutting edge after the allotted holes were drilled.

Referring to Fig. 7, the width 470 of the primary cutting edge 472 of the drill 474 was measured at the peripheral edge of the drill tip.

The drilling was conducted using a single head drilling machine. The drilling was performed on 3-high stacks of laminates (discussed above) with a 0.203 mm (0.008 inch) thick aluminum entry and 1.88 mm (0.074 inch) thick paper core phenolic coated back-up. Drilling 3 laminates at one time is generally standard practice in the industry. The drill tip percent wear was

determined for two drill diameters: 0.35 mm (0.0138 inches) and 0.46 mm (0.018 inches). Both drills were a series 508 tungsten carbide drill available from Tulon Co., Gardenia, California. The chip load during drilling was held constant at 0.001 for each tool. As used herein, "chip load" means the ratio of the drill insertion rate measured in inches per minute to the spindle speed measured in revolutions per minute (rpm). For the 0.35 mm drill, the spindle speed was 100,000 rpm and the insertion rate was 100 inches (254 cm) per minutes. For the 0.46 mm drill, the spindle speed was 80,000 rpms and the insertion rate was 80 inches (203 cm) per minute. A retraction rate of 2.54 m (1000 inches) per minute and a 1.65 mm (0.065 inch) upper drill head limit was held constant for both tool diameters. As use herein, "drill head limit" means the distance that the drill tip was withdrawn above the upper surface of the laminate.

The drill tip percent wear was determined based on a 500 hole drilling pattern shown in Fig. 8 which included 391 holes drilled in a 0.635 cm by 10.16 cm (0.25 inch by 4 inch) block (section 580), followed by 100 holes in a 10 by 10 hole pattern (section 582), followed by 9 holes in a 3 by 3 hole pattern (section 584). The holes in each section were drilled at a hole density of 62 holes per square centimeter (400 hole per square inch). The pattern was repeated three additional times for a total of 2000 holes. The drilling for Tests 1 and 2 was done using a Uniline 2000 single head drilling machine and the drilling for Test 3 was done using a CNC-7 single head drilling machine. Both machines are available from Esterline Technologies, Bellevue, Washington.

Table 2 shows the drill tip percent wear of the drill for Control A and Sample B for the 0.35 and 0.46 mm diameter drills after drilling 2000 holes in the pattern discussed above. Each test was started with a new drill bit.

Table 2

		Control A	Sample B
Test 1 0.35 mm dia. drill	number of tools	3	3
	average drill tip percent wear	28.8	22.2
Test 2 0.46 mm dia. drill	number of tools	20	20
	average drill tip percent wear	34.0	24.4
Test 3 0.46 mm dia. drill	number of tools	10	10
	average drill tip percent wear	30.8	29.3

As can be seen in Table 2, Sample B in Tests 1 and 2, which includes glass fiber filaments coated with a sizing as taught herein that is compatible with laminate matrix resins, exhibited significantly less drill tip percent wear after 2000 holes than Control A, which includes glass fiber filaments that had to be heat cleaned prior to being coated with a silane containing finishing sizing. Test 3 showed only a marginal improvement in drill tip percent wear but it is believed that this is due to the fact that the CNC-7 drilling machine used in this test was older and afforded less control during the drilling test than the Uniline 2000 drilling machine used for Tests 1 and 2.

Locational Accuracy

A common metric used to assess the drilling performance of a laminate is hole locational accuracy. This test measures the deviation in the distance of the actual hole location from its intended location. The measurement was taken on lower surface of the bottom laminate of a 3 laminate stack where the drill exited the laminate stack, since it is expected that this hole location would have the largest discrepancy from the intended or "true" hole location. This difference was assessed in terms of the

"deviation distance", i.e. the distance from the actual true center of the drilled hole on the surface of the laminate to the intended true center of the hole. The deviation distance was measured after the 500 hole sequence discussed above was repeated 4 times, i.e. after each tool drilled a total of 2000 holes. The deviation distance was measured for the last drilled 100 hole pattern, i.e. the last drilled section 582. The holes were drilled using a 0.46 mm (0.018 inch) diameter series 508 drill from Tulon Co. of the type discussed above. As was used in the tool wear test, the spindle speed for the drill was 80,000 rpms and the insertion rate was 80 inches per minute for a chip load of 0.001. The test was repeated eight times for each Control A and Sample B with each test starting with a new drill.

Table 3 shows the result of the locational accuracy test for Control A and Sample B after drilling 2000 holes.

Table 3

	Control A	Sample B
number of drills	8	8
average deviation distance (micrometer)	38	28

As can be seen, Sample B exhibited a lower deviation distance than Control A, which is of particular significance when the laminate is used as an electronic support incorporating a large number of holes and circuits. This is consistent with the drill tip percent wear data shown in Table 2 above. More specifically, it would be expected that laminates that exhibit less drill tip percent wear would also exhibit less deviation distance because the drill tips would be sharper for a longer number of drillings.

EXAMPLE 2

In Example 2, additional drill tool percent wear tests were conducted. Electrical grade laminates Control C and Samples D, E and F incorporating a 7628 style fabric as discussed earlier were tested for drill tool percent wear. The fabric in Control C was 7628-718 fabric from Clark-Schwebel, Inc. The fabrics in Samples D, E and F were woven from fill yarn comprising glass fibers coated with a resin compatible sizing as taught herein and shown in Table 4, and warp yarn having glass fibers coated with a different polymeric matrix material compatible coating composition[104].

[104] The warp yarn was PPG Industries, Inc.'s commercially available fiber glass yarn product designated as G-75 glass fiber yarn coated with PPG Industries, Inc.'s 1383 binder.

Table 4
Weight Percent of Components on Total Solids Basis for Sizing used in Samples D, E and F

	WEIGHT PERCENT OF COMPONENT ON TOTAL SOLIDS BASIS		
	Sample		
COMPONENT	D	E	F
Polyvinyl Pyrrolidone[105]	13.4	14.7	13.4
Cetyl Palmitate[106]	0	29.9	27.3
Epoxy-functional organo silane coupling agent[107]	1.9	1.8	1.6
Acrylic-functional organo-silane coupling agent[108]	3.8	3.7	3.3
Softening Agent[109]	1.9	2.4	2.2
Emulsifying Agent[110]	0	1.6	1.5
Emulsifying Agent[111]	0	3.3	3.0
Antifoaming Agent[112]	0	0.2	0.2
Antifoaming Agent[113]	0.2	0	0
Styrene/Acrylic Copolymer Hollow Particle Dispersion[114]	0	42.4	0
Styrene/Acrylic Copolymer Hollow Particle Dispersion[115]	0	0	38.6

[105] PVP K-30 polyvinyl pyrrolidone which is commercially available from ISP Chemicals of Wayne, NJ.
[106] STEPANTEX 653 which is commercially available from Stepan Company of Maywood, NJ
[107] A-187 gamma-glycidoxypropyltrimethoxysilane which is commercially available from OSi Specialties, Inc. of Tarrytown, NY.
[108] A-174 gamma-methacryloxypropyltrimethoxysilane which is commercially available from OSi Specialties, Inc. of Tarrytown, NY.
[109] EMERY® 6717 partially amidated polyethylene imine which is commercially available from Henkel Corporation of Kankakee, IL.
[110] MACOL OP-10 ethoxylated alkylphenol which is commercially available from BASF Corp. of Parsippany, NJ.
[111] TMAZ-81 ethylene oxide derivative of a sorbitol ester which is commercially available from BASF Corp. of Parsippany, NJ.
[112] MAZU DF-136 antifoaming agent which is commercially available from BASF Corp. of Parsippany, NJ.
[113] SAG 10 antiforming material which is commercially available from OSi Specialties, Inc. of Danbury, Connecticut.
[114] ROPAQUE® HP-1055, 1.0 micron particle dispersion which is commercially available from Rohm and Haas Company of Philadelphia, PA.
[115] ROPAQUE® OP-96, 0.55 micron particle dispersion which is commercially available from Rohm and Haas Company of Philadelphia, PA.

Boron Nitride Dispersion[116]	3.8	0	6.3
Boron Nitride Powder[117]	5.9	0	2.6
Thermoplastic polyester film-forming polymer[118]	23.0	0	0
Thermoplastic polyester film-forming polymer[119]	31.0	0	0
Polyoxyalkylene block copolymer[120]	8.4	0	0
Polyoxyethylated vegetable oil[121]	2.5	0	0
Alkoxylated nonyl phenol[122]	4.2	0	0
LOI	0.35	0.4-0.48	0.34-0.36

The fabrics were subsequently formed into prepregs with an FR-4 epoxy resin having a Tg of about 140°C (designated 4000-2 resin by Nelco International Corporation of Anaheim, CA). The sizing compositions were not removed from the fabric prior to pre-pregging. Laminates were made by stacking 8-plies of the prepreg material and four layers of 1 ounce copper (as shown below) and laminating them together at a temperature of about 355°F (about 179°C), pressure of about 300 pounds per square inch (about 2.1 megaPascals) for about 150 minutes (total cycle time). The thickness of the laminates with copper ranged from about 0.052 inches (about 0.132 cm) to about 0.065 inches (0.165 cm). In forming the laminates, eight prepregs were

---

[116] ORPAC BORON NITRIDE RELEASECOAT-CONC boron nitride dispersion which is commercially available from ZYP Coatings, Inc. of Oak Ridge, TN.
[117] PolarTherm® PT 160 boron nitride powder which is commercially available from Advanced Ceramics Corporation of Lakewood, OH.
[118] RD-847A polyester resin which is commercially available from Borden Chemicals of Columbus, Ohio.
[119] DESMOPHEN 2000 polyethylene adipate diol which is commercially available from Bayer of Pittsburgh, Pennsylvania.
[120] PLURONIC™ F-108 polyoxypropylene-polyoxyethylene copolymer which is commercially available from BASF Corporation of Parsippany, New Jersey.
[121] ALKAMULS EL-719 polyoxyethylated vegetable oil which is commercially available from Rhone-Poulenc.
[122] ICONOL NP-6 alkoxylated nonyl phenol which is commercially available from BASF Corporation of Parsippany, New Jersey.

stacked with copper layers in the following arrangement:

one 1 oz/ft^2 shiny copper layer
three prepreg layers
one 1 oz/ft^2 RTF (reverse treated foil) copper layer
two prepreg layers
one 1 oz/ft^2 RTF copper layer
three prepreg layers
one 1 oz/ft^2 shiny copper layer

The finished laminates were trimmed to 40.6 cm by 50.8 cm (16 inches by 20 inches).

The drilling was conducted using a Uniline 2000 single head drilling machine. The drilling was performed on 3-high stacks of laminates (discussed above) with a 0.010 inch (0.254 mm) thick aluminum entry and 0.1 inch (2.54 mm) thick aluminum clad particle board back-up. The drill tool percent wear was determined for a 0.34 mm (0.0135 inches) tool diameters, series 80 tungsten carbide drill available from Tulon Co., Gardenia, CA. The chip load during drilling was held constant at 0.001, with a spindle speed of 95,000 rpm and insertion rate of 95 inches (241 cm) per minutes. The drill retraction rate was 90 inches (2.29 m) per minute and the upper drill head limit was 0.059 inches (1.5 mm) upper drill head limit.

The drill tip percent wear was examined based on a 1500 and 2500 hole drilling pattern. The holes in each section were drilled at a hole density of 28 holes per square centimeter (about 178 hole per square inch).

Table 2 shows the drill tip percent wear of the for Control C and Samples D, E and F after drilling 1500 and 2500 holes. Each set of holes was started with a new drill bit and each stack of laminates had ten 1500 hole groupings and ten 2500 hole groupings. Three stacks of laminates of each fabric type were drilled so that the drill tip percent wear for 30 drills were measured for each sample.

Table 5

	Drill Tip Percent Wear			
	Control C	Sample D	Sample E	Sample F
1500 holes	24.9	19.8	21.5	19.5
2500 holes	28.3	25.3	28.0	24.3

As can be seen in Table 5, Samples D, E and F, which includes glass fiber filaments coated with a sizing as taught herein that is compatible with laminate matrix resins, exhibited significantly less percent wear after 1500 holes than Control A, which includes glass fiber filaments that had to be heat cleaned prior to being coated with a silane containing finishing sizing. After 2500 holes, the amount of drill tool percent wear for Samples D, E and F is still less than for Control C but less pronounced. This is to be expected since the majority of the tool wear will occur during the earlier drilled holes rather than the last holes drilled in a grouping.

Based in the above, although not limiting in the present invention, it is preferred that prepregs made with glass fiber fabric coated with a polymeric matrix compatible sizing as taught herein have a drilling tip percent wear of no greater than about 32 percent, more preferably no greater than about 30 percent, and most preferably no greater than about 25 percent, as determined after drilling 2000 holes through a stack of 3 laminates, each laminate including eight prepregs, at a hole density of 400 holes per square inch and a chip load of 0.001 with a 0.46 mm (0.018 inch) diameter tungsten carbide drill.

In addition, based in the above, although not limiting in the present invention, it is preferred that prepregs made with glass fiber fabric coated with a polymeric matrix compatible sizing as taught herein have a deviation distance of no greater than about 36 micrometers, more preferably not

greater than about 33 micrometers, and most preferably not greater than about 31 micrometers, as determined after drilling 2000 holes through a stack of 3 laminates, each laminate including eight prepregs, at a hole density of 400 holes per square inch and a chip load of 0.001 with a 0.46 mm (0.018 inch) diameter tungsten carbide drill.

Although not meaning to be bound by any particular theory, it is believed that the presence of a solid lubricant in the glass fiber coating composition disclosed herein, and in one particular embodiment, the presence of the boron nitride, contributes to the improved drilling properties of the laminates of the present invention. More particularly, the solid lubricant contributes to the reduction in drill wear and improvement in locational accuracy of the drilled holes.

Improved drilling properties in laminate made with glass fibers coated with a resin compatible sizing as taught herein provides several advantages. First, longer drill life means that each drill bit can drill more holes before resharpening or disposal. In addition, because the locational accuracy of the holes drilled through the laminates of the present invention is greater than that for conventional laminates, it is expected that more than three laminates can be stacked for drilling at a single time with the same accuracy as that achieved in a 3 laminate stack of conventional laminates. Both of these advantages result is a more cost effective drilling operation. Furthermore, the locational accuracy of the holes drilled in the laminates is improved so that the quality of the electronic support incorporating the laminate in improved.

It will be appreciated by those skilled in the art that changes could be made to the embodiments described above without departing from the broad inventive concept thereof. It is understood, therefore, that this invention is not limited to the particular embodiments disclosed, but it is intended to cover modifications that are within the spirit and scope of the invention, as defined by the appended claims.

WE CLAIM:

1. A prepreg for an electronic support, the prepreg comprising:

(a) a polymeric matrix material; and

(b) a fabric comprising a strand comprising glass fibers, at least a portion of the fabric having a coating which is compatible with the polymeric matrix material, the prepreg having a drill tip percent wear of no greater than about 32 percent, as determined after drilling 2000 holes through a stack of 3 laminates, each laminate including eight of the prepregs, at a hole density of 62 holes per square centimeter (400 holes per square inch) and a chip load of 0.001 with a 0.46 mm (0.018 inch) diameter tungsten carbide drill.

2. The prepreg according to claim 1, wherein the drill tip percent wear is no greater than about 30%.

3. The prepreg according to claim 2, wherein the drill tip percent wear is no greater than about 25%.

4. The prepreg according to claim 1, wherein the polymeric matrix material comprises at least one thermosetting matrix material selected from the group consisting of thermosetting polyesters, vinyl esters, epoxides, phenolics, aminoplasts, thermosetting polyurethanes and mixtures thereof.

5. The prepreg according to claim 4, wherein the polymeric matrix material comprises at least one thermoplastic matrix material selected from the group consisting of polyolefins, polyamides, thermoplastic polyurethanes, thermoplastic polyesters, vinyl polymers, polyimides, polyether sulfones, polyphenyl sulfones, polyetherketones, polyphenylene oxides, polyphenylene sulfides, polyacetals, polycarbonates and mixtures thereof.

6. The prepreg according to claim 1, wherein at least one of the glass fibers is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and combinations thereof.

7. The prepreg according to claim 1, wherein the coating comprises solid lubricant particles.

8. The prepreg according to claim 7, wherein the solid lubricant particles comprise at least one non-hydratable inorganic solid lubricant particle selected from the group consisting of graphite, boron nitride, metal dichalcogenides, cadmium iodide, silver sulfide, indium, thallium, tin, copper, zinc, gold, silver, calcium carbonate, calcium fluoride, zinc oxide, molybdenum disulfide, molybdenum diselenide, tantalum disulfide, tantalum diselenide, tungsten disulfide, tungsten diselenide and mixtures thereof.

9. The prepreg according to claim 8, wherein the non-hydratable inorganic solid lubricant particles comprise hexagonal crystal structure boron nitride particles.

10. The prepreg according to claim 7, wherein a hardness value of the solid lubricant particles is less than or equal to a hardness value of the E-glass fibers.

11. The prepreg according to claim 1, wherein the laminate comprises eight plies of woven fabric style selected from the group consisting of style 106, style 108, style 1080, style 2113, style 2116, style 7535 and style 7628 and combinations thereof.

12. The prepreg according to claim 1, wherein the coating comprises (1) polyester; (2) at least one polymer selected from the group consisting of vinyl pyrrolidone polymers, vinyl alcohol polymers and starches; and boron nitride particles.

13. The prepreg according to claim 1 wherein the coating comprises a plurality of discrete, dimensionally stable particles formed from materials selected from the group consisting of organic materials, polymeric materials, composite materials and mixtures thereof that provide an interstitial space between at least one fiber and at least one adjacent fiber, the particles having an average particle size of about 0.1 to about 5 micrometers;

14. The prepreg according to claim 13, wherein at least one of the particles comprises a polymeric material selected from the group consisting of inorganic polymeric materials, synthetic organic polymeric materials, semisynthetic organic polymeric materials and natural organic polymeric materials.

15. The prepreg according to claim 14, wherein the at least one particle comprises a thermoplastic organic polymeric material selected from the group consisting of acrylic polymers, vinyl polymers, thermoplastic polyesters, polyolefins, polyamides, thermoplastic polyurethanes and mixtures thereof.

16. The prepreg according to claim 15, wherein the at least one particle is formed from an acrylic copolymer which is a copolymer of styrene and acrylic.

17. The prepreg according to claim 16, wherein the particles are first particles and the resin compatible coating composition further comprises a plurality of additional discrete, dimensionally stable particles different from the first particles selected from the group consisting of metals, graphite, oxides, carbides, nitrides, borides, sulfides, silicates and carbonates.

18. The prepreg according to claim 13, wherein the coating comprises a lubricant selected from the group consisting of cetyl palmitate, cetyl laurate, octadecyl laurate, octadecyl myristate, octadecyl palmitate, octadecyl stearate and paraffin.

19. The prepreg according to claim 13, wherein the particles comprise boron nitride particles and hollow particles formed from a copolymer of styrene and acrylic.

20 The prepreg according to claim 1 wherein at least one of the glass fibers is at least partially coated with the coating.

21. The prepreg according to claim 1 wherein the fabric is selected from the group consisting of woven fabrics, nonwoven fabrics, knitted fabrics and mats.

22. The prepreg according to claim 1 wherein the prepreg has a deviation distance of no greater than about 36 micrometers, as determined after drilling 2000 holes through a stack of 3 laminates, each of the laminates including eight of the prepregs, at a hole density of 62 holes per square centimeter (400 holes per square inch) and a chip load of 0.001 with a 0.46 mm (0.018 inch) diameter tungsten carbide drill.

23. The prepreg as in claim 1 wherein at least a portion of the fabric comprises twisted glass fiber yarn.

24. The prepreg as in claim 1 wherein at least a portion of the fabric comprises non-twisted glass fibers.

25. The prepreg as in claim 1 wherein the at least one glass fiber is manufactured using a direct melt glass fiber forming process.

26. The prepreg as in claim 1 wherein the least one glass fiber is manufactured using a marble melting glass fiber forming process.

27. The prepreg as in claim 1 wherein the fabric is a non-woven fabric.

28. The prepreg as in claim 1 wherein the fabric is a woven fabric.

29. The prepreg as in claim 28 wherein the fabric is woven on an air jet loom.

30. The prepreg as in claim 29 wherein the at least one glass fiber is manufactured using a direct melt glass fiber forming process and at least a portion of the fabric comprises twisted glass fiber yarn.

31. The fabric as in claim 28 wherein the fabric is woven on a rapier loom.

32. The fabric as in claim 31 wherein the at least one glass fiber is manufactured using a direct melt glass fiber forming process and at least a portion of the fabric comprises twisted glass fiber yarn.

33. The fabric as in claim 31 wherein the at least one glass fiber is manufactured using a marble melt glass fiber forming process and at least a portion of the fabric comprises non-twisted glass fibers.

34. A laminate incorporating the prepreg according to clam 1.

35. A prepreg for an electronic support, the prepreg comprising:

(a) a polymeric matrix material; and

(b) a woven reinforcement fabric comprising a glass fibers, at least a portion of the fabric having a coating which is compatible with the polymeric matrix material, the prepreg having a deviation distance of no greater than about 36 micrometers, as determined after drilling 2000 holes through a stack of 3 laminates at a hole density of 62 holes per square centimeter (400 holes per square inch) and a chip load of 0.001 with a 0.46 mm (0.018 inch) diameter tungsten carbide drill.

36. The prepreg according to claim 35, wherein the deviation distance is no greater than about 33 micrometers.

37. The prepreg according to claim 36, wherein the deviation distance is no greater than about 31 micrometers.

38. The prepreg according to claim 35, wherein the polymeric matrix material comprises at least one thermosetting matrix material selected from the group consisting of thermosetting polyesters, vinyl esters, epoxides, phenolics, aminoplasts, thermosetting polyurethanes and mixtures thereof.

39. The prepreg according to claim 38, wherein the polymeric matrix material comprises at least one thermoplastic matrix material selected from

the group consisting of polyolefins, polyamides, thermoplastic polyurethanes, thermoplastic polyesters, vinyl polymers, polyimides, polyether sulfones, polyphenyl sulfones, polyetherketones, polyphenylene oxides, polyphenylene sulfides, polyacetals, polycarbonates and mixtures thereof.

40. The prepreg according to claim 35, wherein at least one of the glass fibers is selected from the group consisting of E-glass fibers, D-glass fibers, S-glass fibers, Q-glass fibers, E-glass derivative fibers, and combinations thereof.

41. The prepreg according to claim 35, wherein the coating comprises solid lubricant particles.

42. The prepreg according to claim 41, wherein the solid lubricant particles comprise at least one non-hydratable inorganic solid lubricant particle selected from the group consisting of graphite, boron nitride, metal dichalcogenides, cadmium iodide, silver sulfide, indium, thallium, tin, copper, zinc, gold, silver, calcium carbonate, calcium fluoride, zinc oxide, molybdenum disulfide, molybdenum diselenide, tantalum disulfide, tantalum diselenide, tungsten disulfide, tungsten diselenide and mixtures thereof.

43. The prepreg according to claim 42, wherein the non-hydratable inorganic solid lubricant particles comprise hexagonal crystal structure boron nitride particles.

44. The prepreg according to claim 41, wherein a hardness value of the solid lubricant particles is less than or equal to a hardness value of the E-glass fibers.

45. The prepreg according to claim 35, wherein the laminate comprises eight plies of woven fabric style selected from the group consisting of style 106, style 108, style 1080, style 2113, style 2116, style 7535 and style 7628 and combinations thereof.

46. The prepreg according to claim 35, wherein the coating comprises (1) polyester; (2) at least one polymer selected from the group consisting of vinyl pyrrolidone polymers, vinyl alcohol polymers and starches; and boron nitride particles.

47. The prepreg according to claim 35 wherein the coating comprises a plurality of discrete, dimensionally stable particles formed from materials selected from the group consisting of organic materials, polymeric materials, composite materials and mixtures thereof that provide an interstitial space between at least one fiber and at least one adjacent fiber, the particles having an average particle size of about 0.1 to about 5 micrometers;

48. The prepreg according to claim 47, wherein at least one of the particles comprises a polymeric material selected from the group consisting of inorganic polymeric materials, synthetic organic polymeric materials, semisynthetic organic polymeric materials and natural organic polymeric materials.

49. The prepreg according to claim 48, wherein the at least one particle comprises a thermoplastic organic polymeric material selected from the group consisting of acrylic polymers, vinyl polymers, thermoplastic polyesters, polyolefins, polyamides, thermoplastic polyurethanes and mixtures thereof.

50. The prepreg according to claim 49, wherein the at least one particle is formed from an acrylic copolymer which is a copolymer of styrene and acrylic.

51. The prepreg according to claim 50, wherein the particles are first particles and the resin compatible coating composition further comprises a plurality of additional discrete, dimensionally stable particles different from the first particles selected from the group consisting of metals, graphite, oxides, carbides, nitrides, borides, sulfides, silicates and carbonates.

52. The prepreg according to claim 47, wherein the coating comprises a lubricant selected from the group consisting of cetyl palmitate, cetyl laurate, octadecyl laurate, octadecyl myristate, octadecyl palmitate, octadecyl stearate and paraffin.

53. The prepreg according to claim 47, wherein the particles comprise boron nitride particles and hollow particles formed from a copolymer of styrene and acrylic.

54. The prepreg according to claim 35 wherein at least one of the glass fibers is at least partially coated with the coating.

55. The prepreg according to claim 35 wherein the fabric is selected from the group consisting of woven fabrics, nonwoven fabrics, knitted fabrics and mats.

56. A laminate incorporating the prepreg according to claim 35.

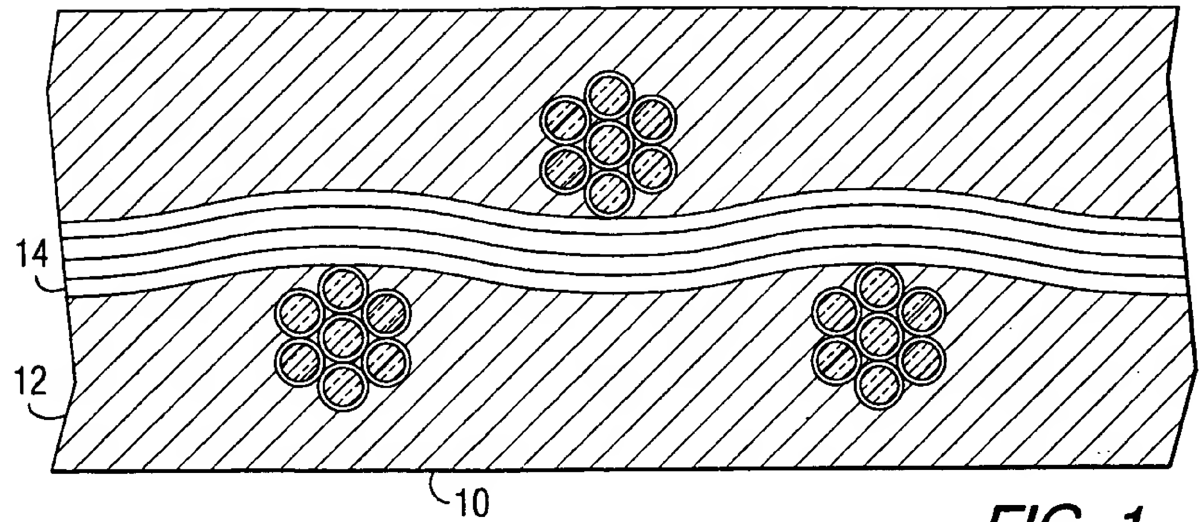


FIG. 1

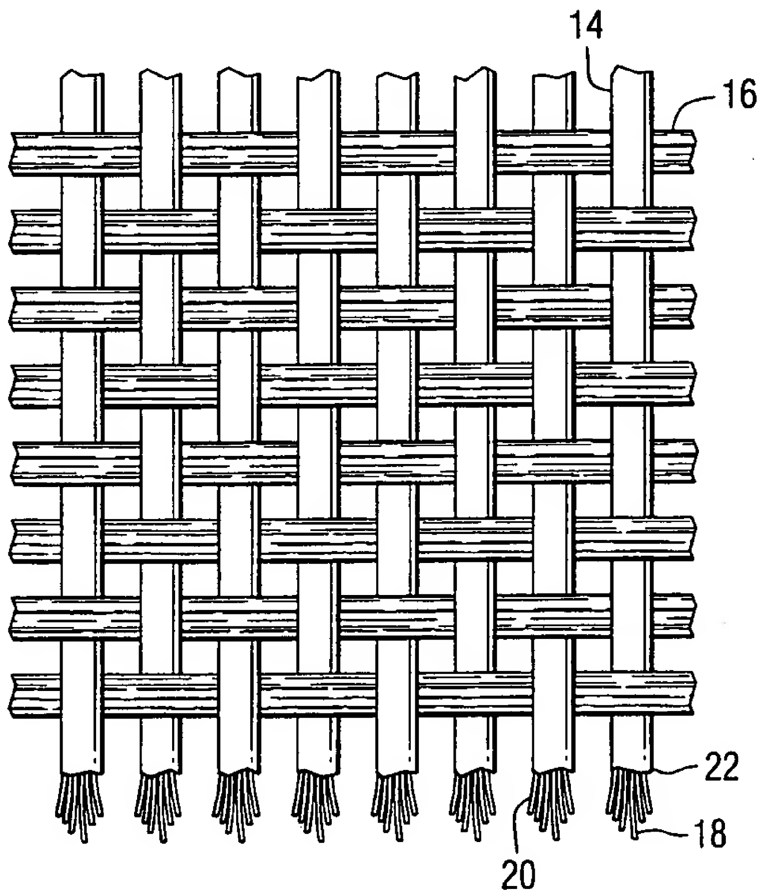


FIG. 2

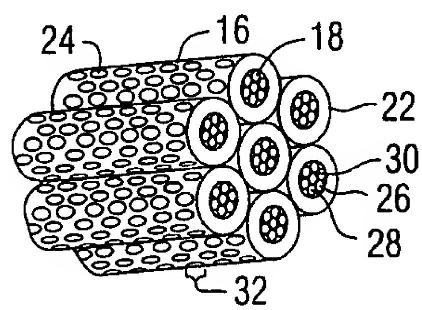


FIG. 3

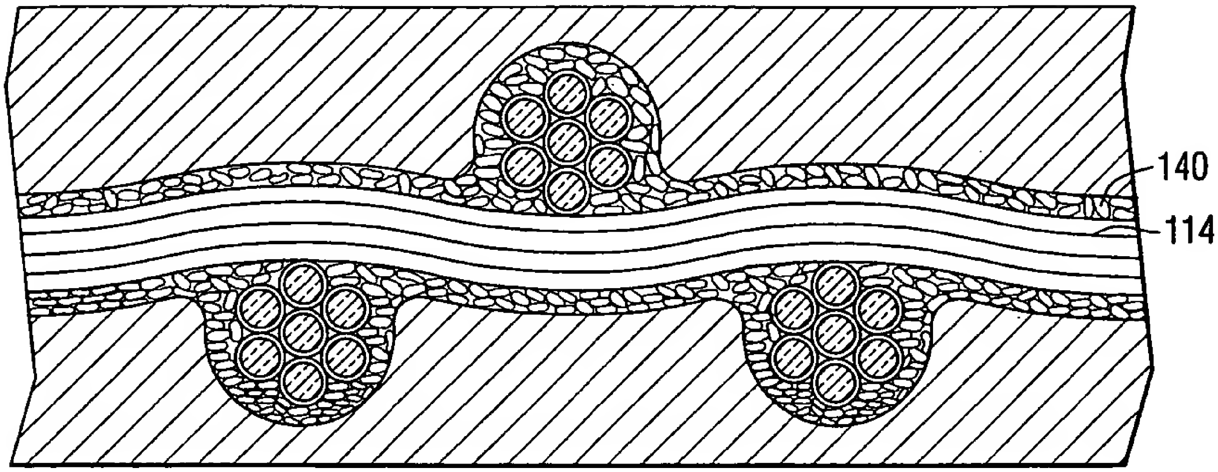


FIG. 4

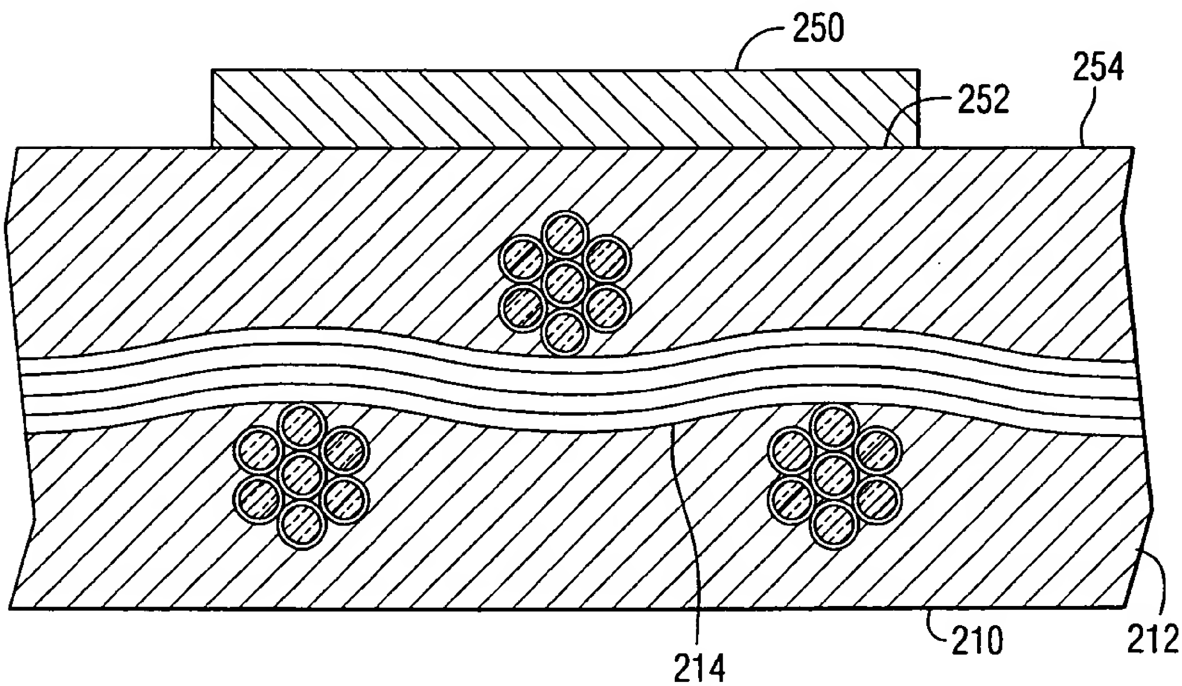


FIG. 5

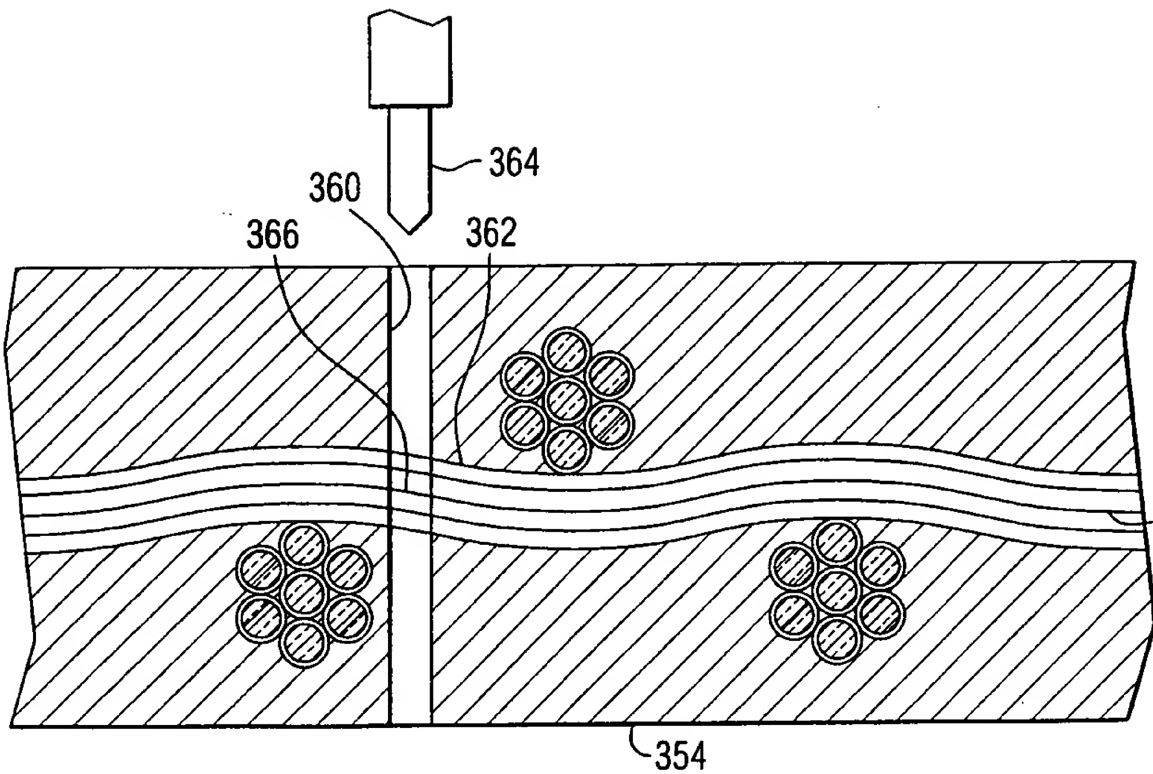


FIG. 6

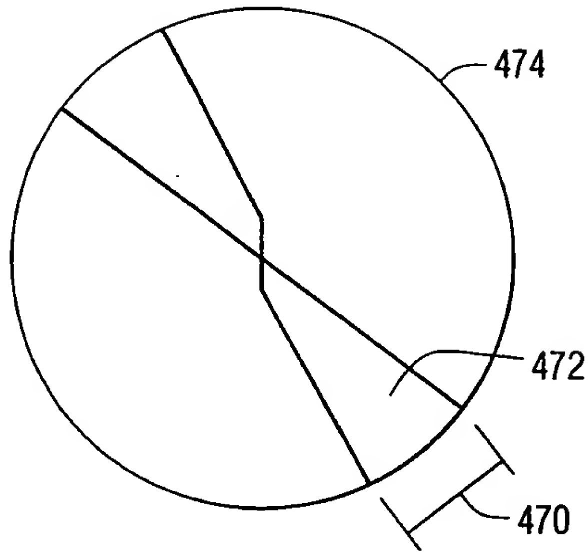


FIG. 7

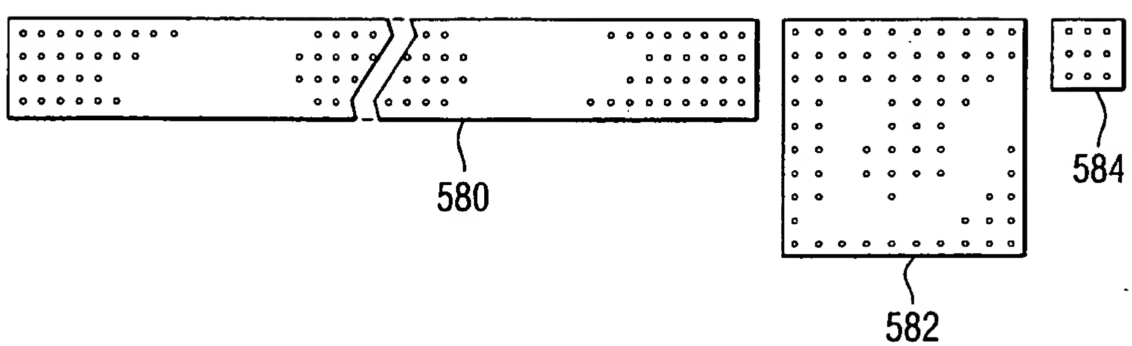


FIG. 8

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/21443

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03C25/10 C08J5/08 H05K1/03

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C03C C08J H05K F16D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96 39364 A (PPG INDUSTRIES INC.) 12 December 1996 (1996-12-12) page 5, line 1 - line 13 ---	1-56
X	US 5 284 807 A (KOMORI KIYOTAKA ET AL) 8 February 1994 (1994-02-08) column 1, line 55 - line 66 ---	1-56
X	US 5 593 767 A (YAMANAKA HIROYUKI ET AL) 14 January 1997 (1997-01-14) table 2 --- -/--	1-6,11, 20-40

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 March 2000	16/03/2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Reedijk, A

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 99/21443

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
P,X	DATABASE INSPEC 'Online! INSTITUTE OF ELECTRICAL ENGINEERS, STEVENAGE, GB NOVICH B E: "Hybon RCY yarns: a laminate reinforcement developed for printed circuit boards" Database accession no. 6242125 XP002129290 abstract & CIRCUITREE, MARCH 1999, CIRCUITREE, USA, vol. 12, no. 3, page 44, 46, 51 ISSN: 1059-843X	1-56
A	WO 90 01860 A (TELDIX GMBH) 22 February 1990 (1990-02-22) claims	1-56
A	US 3 312 569 A (T.E. PHILIPPS ET AL.) 4 April 1967 (1967-04-04) cited in the application claims	1-56
A	US 5 217 778 A (G.J. LACHASSE) 8 June 1993 (1993-06-08) cited in the application abstract	1-56
A	DATABASE WPI Section Ch, Week 9706 Derwent Publications Ltd., London, GB; Class A85, AN 97-060830 XP002106571 & JP 08 309928 A (HITACHI CHEM CO LTD), 26 November 1996 (1996-11-26) abstract	1-56
A	US 5 236 777 A (H.INOGUCHI ET AL.) 17 August 1993 (1993-08-17) cited in the application the whole document	1-56
A	WO 97 35457 A (ALLIED SIGNAL INC) 25 September 1997 (1997-09-25) example 1	1-56
A	EP 0 468 476 A (MITSUBISHI GAS CHEMICAL CO) 29 January 1992 (1992-01-29) page 2, line 13 - line 58	1-56